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Technical optimization of biogas plants to deliver demand oriented power

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Nomenclature

Mathematical Symbols and variables

$\dot{\gamma}$	shear rate
η	dynamic viscosity
ν	speed
ρ	density
σ^2	variance
$\triangle G$	Gibbs free energy
$\triangle r$	variation of the rope length
$^{\circ}C$	degree Celsius
A	inequality constraints matrix
ACN	C/N ratio matrix
ADM	dry matter matrix
ADM_i	average dry matter fed until interval i in 24 hours from m different substrates
Aeq	equality constraints matrix
AGS	gas storage range matrix
$AHRT$	hydraulic residence time matrix
AMS	minimum substrate quantity matrix
AN	ammonia inhibition matrix
$AOLR$	organic loading rate matrix
ATE	total energy vector

b	inequality constraints vector
bCN	C/N ratio vector
bDM	dry matter vector
beq	equality constraints vector
$bGSMax$	maximum gas storage range vector
$bGSMin$	minimum gas storage range vector
$bHRT$	hydraulic residence time vector
$bMaxOLR$	maximum organic loading rate vector
$bMinOLR$	minimum organic loading rate vector
bMS	minimum substrate quantity vector
bN	ammonia inhibition vector
$bpriceorg$	cost of the substrates fed in the optimization interval by a continuous feeding
bTE	energy required to deliver the requested load
C/N_i	C/N ratio in the interval i
$C/Nref$	C/N ratio reference value
C_i	carbon quantities of m different substrates fed in the interval i
c_j	carbon content substrate j
$CF(T,P)_i$	volume correction factor for temperature pressure and water content
$CHPef$	engine electrical efficiency
d	required energy vector
D_{ref}	maximum input dry matter
$digestervol$	volume of digestates in the digester in m^3
DM	dry matter quantities of m different substrates fed in the interval i
dm_j	dry matter substrate j
$e_{j,t}$	energy production from the j substrate at a time t

E_j	energy production curve from the j substrate
$G(30s)_i$	gas production in 30 s
$G(hour)_i$	hourly gas production
$g_{j,t}$	biogas yield of the substrate j, at a time t
$GCHP_i$	CHP gas consumption
GE_i	Energy generated by substrates fed in the optimization interval [1,t] at the time i
GS_0	addition of the initial gas storage volume of the different tanks
GS_i	addition of the gas volumes at standard conditions at interval i
h	height of the cap
HP	height of gas production peak
HRT_i	hydraulic residence time at the interval i
Hz	hertz
J	Joule
K	volume ratio between digester and storage
kg	kilogram
kW	kilowatt
L_j	length of biogas yield curve data series of the substrate j
lb	minimum substrate quantity vector
m	number of substrates available for feeding
m^3	cubic meter
M_0	methane content of gas storage before the optimizaion interval
M_j	average methane content of j substrate
$M_{pH=5to4.4}$	additional acid required to reach pH 4.4
$M_{pH=5}$	amount of acid to reach pH 5
MAN	maximum allowed nitrogen

$MaxOLR$	maximum organic loading rate
$MaxS$	maximum allowed gas storage
$MHRT$	minimum hydraulic residence time
$MinOLR$	minimum organic loading rate
$MinS$	minimum allowed gas storage
$MOLR$	maximum sustainable organic loading rate
n	number of subsamples
N_i	nitrogen fed in an interval i from m different substrates
n_j	nitrogen concentration substrate j
Nob	Number of observations
NS_j	updated biogas yield curve or step response from substrate j
O_i	substrates organic dry matter fed in the interval i
oDM	organic dry matter
odm_j	organic dry matter substrate j
OLR_i	organic loading rate in the interval i
P	energy matrix
P_{aD}	air pressure between digester membranes
P_{aS}	air pressure between storage membranes
P_{atm}	atmospheric pressure
$P_{g\,k,i}$	gas pressure of tank k at interval i
P_{gD}	pressure gas digester
P_{gS}	pressure gas storage
P_{pipe}	pipe pressure
pGE	energy generated from the feedings prior to the optimization interval
Q_j	vector with the quantities of substrate j

R	sphere radius
r	tank radius
RL_i	required load at time i
rpm_D	revolution per minute fan digester
rpm_S	revolution per minute fan storage
S_j	biogas yield curve or step response from substrate j
t	time
$T_{g\ k,i}$	gas temperature of tank k at interval i
TN	273.15°K
TN_i	average nitrogen fed until interval i in 24 hours from m different substrates
TVM_i	total gas volume measured at interval i
ub	maximum substrate quantity vector
$V_{k,i}$	gas volume at operating conditions of tank k at interval i
$V_{subsample}$	subsample volume
$V_{trapped}$	air volume between three valves
$VM_{k,i}$	gas volume measured of tank k at interval i
VN_S	gas volume at standard conditions of storage
VN_D	gas volume at standard conditions of digester
$VN_{k,i}$	gas volume at standard conditions of storage k at interval i
$Vprice$	price vector
$WP(T_{g\ k,i})$	water vapor correction factor based on gas temperature of tank k at interval i
x	vector substrate quantities
X_i	quantities of m different substrates fed in an interval i
$x_{j,i}$	quantity of substrate j fed in the intervall i

Chemical compounds

C	carbon
CH_3CH_2OH	ethanol
CH_3COO^-	acetate
CH_4	methane
Co	cobalt
CO_2	carbon dioxide
$CoCl_26H_2O$	cobalt dichloride hexahydrate
Cu	copper
Fe	iron
H_2	hydrogen
H_2O	Water
H_2S	hydrogen sulphide
Mn	manganese
Mo	molybdenum
N	nitrogen
NH_3	free ammonia
$NH_4 - N$	ammonium nitrogen
NH_4^+	ammonium ion
Ni	nickel
$NiCl_26H_2O$	nickel chloride hexahydrate
P	phosphorous
Se	selenium
Zn	zinc

Abreviations

Re	Reynolds number
rpm	revolution per minute
RSD	relative standard deviation
ADM1	Anaerobic digestion model No 1
AT	activity test
BMP	biochemical methane potential
CCM	Corn Cob Mix
CHP	combined heat and power
COD	chemical oxygen demand
CSTR	continuous stirred tank reactors
DM	dry matter
EPEX SPOT SE	european power exchange
FOS/TAC	is equivalent to VFA/TIC but in german language
HRT	hydraulic residence time
OLR	organic loading rate
ppm	parts per million
PV	photovoltaic
SRT	solid residence time
TIC	total inorganic carbon
TOS	theory of sampling
UASB	upflow anaerobic sludge blanket
VFA	volatile fatty acids

Abstract

The increasing share of alternating renewable energies from wind and solar introduces the necessity of flexible power generation to reduce the gap between production and demand. Flexible power generation can be provided by fossil fuels but in the long term it should be provided by renewable energies. Biogas plants can provide flexible power generation in a wide range but the existing plants are designed to provide base load.

Flexible power generation can be improved by increasing gas storage capacity, but the ability to provide a load profile is limited. A further improvement is achieved by changing the current continuous feeding to feeding on demand where the biogas plant is fed according to load requirements.

Three technical aspects were identified in this thesis to improve the flexible power potential of existing plants using feeding on demand; online monitoring, improved gas volume measurements and feeding model. These were implemented in a full-scale biogas plant.

Changed feeding schedule may generate process disturbances that require rapid detection to provide certainty to the operator and avoid economic losses. A digester is a highly heterogeneous system in distribution and composition making samples unrepresentative. An online monitoring system was developed and patented, implementing the guidelines of sampling theory. Possible bias generated by the operator is avoided and a higher density of data is obtained.

Gas volume measurement improvements were achieved, including the development of a gas management system to optimize the existing storage.

A prediction model of biogas generation kinetics was developed based on heuristic knowledge, updated based on the system response. Mathematical description was achieved but for implementation further improvements of gas volume determination are required to accurately calculate gas production.

Improvements developed in this thesis make plant operation simpler and more certain; their use could optimize at least 2.73 GW flexible power in Germany.

Abstrakt

Der zunehmende Anteil alternativer erneuerbarer Energien aus Wind und Sonne erhöht die Notwendigkeit einer flexiblen Stromerzeugung, um die Differenz zwischen Produktion und Nachfrage zu verringern. Die Stromerzeugung kann flexibel durch fossile Brennstoffe erfolgen, langfristig sollte dies jedoch aus erneuerbaren Energien stammen. Biogasanlagen könnten eine flexible Stromerzeugung in einem hohen Maß gewähren, aber die vorhandenen Anlagen sind nur für die Grundlast ausgelegt.

Die flexible Stromerzeugung kann durch Erhöhung der Gasspeicherkapazität verbessert werden, dennoch ist die Bereitstellung eines Lastprofils begrenzt. Eine zusätzliche Verbesserung wäre die Änderung der aktuellen kontinuierlichen Fütterung in eine bedarfsabhängige Fütterung, bei der die Biogasanlage entsprechend den Lastanforderungen des Netzbetreibers gefüttert wird.

In dieser These wurden drei technische Aspekte (Online Überwachung, verbesserte Gasvolumenmessungen und Fütterungsmodell) identifiziert, um das flexible Energiepotenzial bestehender Anlagen durch die bedarfsabhängige Fütterung zu verbessern. Dieses wurde bereits auf einer kommerziellen Biogasanlage umgesetzt.

Ein geänderter Fütterungsplan kann Prozessstörungen verursachen, die eine schnelle Erkennung erfordern um dem Betreiber eine Sicherheit zu geben und wirtschaftliche Verluste zu vermeiden. Ein Fermenter ist hinsichtlich des Mischverhaltens und unterschiedlicher Fermentationsstadien ein sehr heterogenes System, weshalb die Proben nicht repräsentativ sind. Es wurde ein Online-Überwachungssystem entwickelt und patentiert, das sich nach der Probeentnahme Theorie richtet. Durch das Anwenden des Systems vermeidet man eine mögliche Verzerrung der Analyse durch den Betreiber und erhält eine höhere Datendichte.

Eine Verbesserung der Gasvolumenmessung wurde erreicht mit der Entwicklung eines Gasmanagementsystems, dass die vorhandene Gasspeicherung optimiert.

Basierend auf heuristischem Wissen wurde ein Vorhersagemodell für die Biogaserzeugungskinetik entwickelt, das sich abhängig von der Systemanforderung aktualisiert. Ein mathematisches Modell wurde hergeleitet, jedoch für die Implementierung sind weitere Verbesserungen der Gasvolumenmessung notwendig, um die Gasproduktion genau zu berechnen.

In dieser Arbeit entwickelte technische Verbesserungen sorgen für einen einfachen und sicheren Betrieb der Anlage. Der Einsatz dieses Systems könnte in Deutschland mindestens 2,73 GW flexibler Leistung aus Biogasanlagen optimieren.

1. Introduction

1.1. Background

According to the German Renewable Energy Act (2017), the percentage of renewable energy technologies as a part of all electricity production in Germany should be between 40 - 45% by 2025 and 55 - 65% by 2035. In order to achieve this target, technologies with the lowest levelized cost of energy are chosen, such as wind and PV [1]. From 2017 to 2019 the expansion of new biomass plants was limited to 150 MW per year. Within the same period, the limits for PV are 2500 MW per year, onshore wind 2800 and offshore wind 6000 MW per year.

This large increase of intermittent renewable energy producers makes it necessary to introduce or promote technologies to balance production and demand. These technologies are flexible power plants, demand side management, storage technologies and grid extension[2, 3]. Within renewable technologies biogas plants have the advantage in that they have their own storage and therefore power production is flexible. Power supply can be provided when the highest demand is required and reduced in periods of overproduction.

In addition, power production for biogas plants does not depend on weather conditions. This can be observed after comparing the electricity generated to the installed capacity of different renewable energies in Germany in 2016. According to [4], the largest producer was wind energy with 77.4TWh generated with an installed capacity of 49.5GW followed by solar PV with 38.2TWh generated with an installed capacity of 41.3GW. Biogas plants in comparison had generated 34.6TWh with an installed capacity of about 5.72GW. The resultant average load factor[1] of : wind 17.8%, solar PV 10.5% and biogas 69.2%. The higher load factor of biogas indicates a larger percentage of hours producing at nominal capacity compared with intermittent renewable energy producers like PV or Wind.

The benefits of producing power on demand with biogas plants has been presented in many studies. In [5], it is shown that biogas plants are a cost-effective option for improving the integration of intermittent renewable energy systems due to its capacity to reduce surplus energy when required. Also the cost of additional flexible options can be reduce by flexible biogas plants. Similar results are presented in [6] where a potential reduction up to 30 % in daily residual load can be obtained

[1] i.e for the wind generation 77200 GWh/(8760h*49.5GW) = 17.8%

by flexible operating the existing bioenergy plants in the TransnetBW transmission system. In [7], it is shown that flexible operated plants can reduce the need for grid expansion.

Furthermore, the green-house emissions from biogas plant-derived electricity is significantly lower than gas steam power stations, another alternative that is used to provide flexible power [1]. This study considers the flexible operation of biogas plants with constant biogas production and endless gas storage.

Biogas plants can also receive economical benefits by changing to a flexible biogas operation under the German Renewable Energy Act [8]. Flexible biogas operation is mandatory for the successful implementation of biogas plants in countries where there is not a Fixed feed-in tariffs support schemes and the plants are forced to produce when the electricity price is high in order to be economically feasible.

The ability to generate power on demand is required to improve the economical feasibility of the existing power plants and it is mandatory for the development of future projects within the Renewable Energy Act in Germany.

Two main alternatives to improve the capacity of existing biogas plants that deliver balancing power are presented in [9]:

- *Biogas storing concepts*. These include an increase of the existent gas storage capacity or the use biogas upgrading units to transform biogas to biomethane. The first concept of increased gas storage capacity was found in [9] as the best suited configuration to supply flexible power generation in the short term. The second concept includes biogas upgrading units which implies a higher investment and depends on the local net conditions. The main advantage is the access to the large gas storage usually available in the gas grid, which will decouple between biogas generation and use.
- *Feeding on demand*. This consists of modifying the feeding program in order to change the biogas production when it is required. The existing gas storage capacity can be saved for over-production events from other renewable energies like wind or solar or to increase the ability to deliver a high variable load profile. There are two alternatives to generate flexible biogas production: using the existent digester configuration or modifying it, including additional fixed bed reactors to ferment the liquid fraction after hydrolysis. These reactors have been shown to be stable and have fast biogas production response after a feeding [10]. The focus of this work is conventional biogas plants. The fixed bed reactors will not be examined in this study. With the help of feeding on demand the need of an expanded biogas storage is decreased or avoided, making this alternative economically attractive.

The main obstacle to exploit this potential is that the existing plants are not designed for flexible energy generation. Prevailing design parameters are: substrate characteristics and availability (which determine the electrical output and digester volume), heat (self-consumption and possible heat use concept) and digestate usage

(chemical composition of the fertilizer to determine the irrigation area). Hourly electricity prices or variable electricity power requirements (load profiles) are not considered in the design. The feeding program is characterized by an even distribution of the substrate as the largest economic benefit was given by a constant electricity production at its maximum power. The gas storage is a buffer of the production and its volume measurements are not accurate.

1.2. Problem statement

In order to maximize the flexible biogas power potential of the existing plants using feeding on demand it is necessary to overcome the following technical aspects:

Feeding model: Current biogas feeding programs are characterized by constant and equally distributed substrate quantities in time. As a result, the biogas production is almost constant and they provide base-load. It has been shown by [11, 12, 13, 14, 15] that flexible biogas production can be generated by modifying the feeding program of the plant. Feeding programs are based on model predictions which need extensive calibration which is not always practical at the biogas plants.

Online monitoring: changes in the feeding program can generate process imbalances that must be detected on time to avoid large disturbances on the biological process and the possible economical loss.

Gas storage: Gas holders are intended to buffer the biogas production and store the gas during maintenance for that reason, the volume accuracy and storage capacity of gas holders are not of major importance [16]. Weather effects are not considered and it can generate loss of biogas especially at high filling levels.

1.3. Objectives

In order to provide a solution to the problem the objectives are defined as follows:

- Develop a heuristic biogas model that enables the generation of feeding programs restricted by commonly used parameters of the biogas industry. Feeding programs should optimize the usage of the existing gas storage allowing the plant to deliver a wider range of loads as well as to provide system services, such as offering control power in balancing markets.
- Develop an online monitoring system that allows the continuous supervision of the biological process. Sampling acquisition should be representative for the digester, automatic, and able to generate high data density. Online measurements should be adequate to characterize the stability of the anaerobic digestion process.
- Improve gas storage volume measurements and define operating ranges where the measurements are accurate and weather effects are minimized.

2. Material

2.1. Anaerobic digestion

This is a biological process in which organic materials are decomposed through the cooperation of different bacterial and archaeal groups in the absence of oxygen. In the process large organic molecules are broken down into smaller single molecules producing biogas and digestates as final products. Biogas is a gas mixture of different gases; methane CH_4(50-70%), carbon dioxide CO_2(30-50%), hydrogen sulfide (in ppm), and other trace gases. Composition of the different fractions depends on the feedstock characteristics [17]. Digestate, on the other hand, is a mixture of difficult to degrade organic substances (lignin) and inorganic residues (salts). Its nutrient content also depends on the characteristics of the inputs. In comparison with manure due to the high degree of mineralization of digestate, its nutrients are easily available for the soil improving their characteristics as a fertilizer [18].

2.1.1. Operating Temperature

Biogas process can be developed at 3 temperature ranges.

Themophilic 55-60 $^{\circ}C$

Mesophilic 35-40$^{\circ}C$

Psychrophilic <30$^{\circ}C$

Fermentation processes are faster at high temperatures and for that reason in many commercial applications Hydraulic Residence Time (HRT) is reduced decreasing digester size and investment cost. The number of microorganisms at thermophilic conditions is lower compared with mesophilic conditions which makes the system more sensitive to temperature changes (allowed temperature variation±1°C). On the other hand, the number of microorganisms in the mesophilic temperature range is much larger, which makes the process more stable. Temperature variations of ±3°C are possible without a big change in biogas production [19, 20]. Due to the low degradation speed psychrophilic conditions are not normally used in industrial operations[18].

Digestion in mesophilic conditions is a more robust and stable process than in thermophilic conditions not dependent on feedstock chemical composition and Organic Loading Rate (OLR), see sec. 2.1.4[21].

Tests and measurements developed in this work were done on a digester operating at mesophilic conditions.

2.1.2. Stages of anaerobic digestion

The anaerobic digestion process is divided into 4 distinct reaction, in which 5 main trophic groups of bacteria are identified. Optimum pH ranges for hydrolytic acidogenic bacteria are between 4.7 to 7 while for methanogenic archae the range is between pH 6.8 -7.8. These ranges imply that in a single tank reactor it is necessary to compromise to keep the conditions favorable for all microorganisms. On the other hand, a cascade system of two tanks has the advantage of allowing optimum conditions for each microorganism; however in the first tank, hydrolysis gas is produced and requires treatment to avoid negative environmental consequences and safety risks [22]. Fig. 2.1 presents the stages of anaerobic digestion divided for one and two steps process.

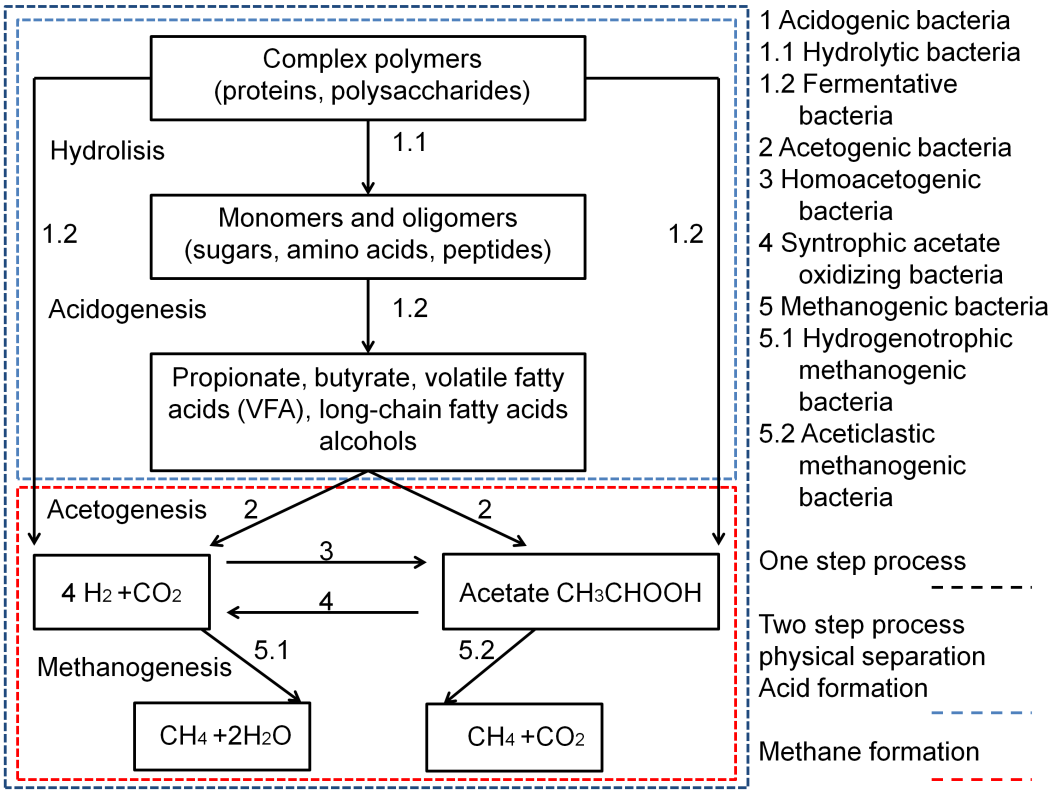

Figure 2.1.: Steps of biogas production and bacteria trophic groups involved. Adapted from [23], [20],[24]

Hydrolysis. Hydrolysis is the decomposition of molecules in water. In this step hydrolytic acidogenic bacteria produce enzymes (amylases, proteases, and lipases)

to decompose insoluble organic compounds, such as carbohydrates, proteins, and fats into soluble sugars, amino acids, and long chain fatty acids.

It is important to differentiate the above chemical definition of hydrolysis from the first step of a two-step anaerobic digestion plant. Two step plants have a hydrolysis tank which is operated at a low pH (normally 5.5 - 6) to improve degradation conditions and avoid methane generation. In this tank, hydrolysis gas ($H_2 + CO_2$) is produced, together with fatty acids and alcohol. This is therefore a large part of the acidogenesis step.

The rate of hydrolysis depends on particle size, pH, enzyme production, and diffusion and adsorption of enzymes by organic compounds[24]. The decomposition of cellulose and hemicellulose is a main factor slowing organic fermentation.

Acidogenesis.

In this step, fermentative (acid forming) bacteria transform hydrolysis products into hydrogen H_2,carbon dioxide CO_2, alcohol and short chain fatty acids (formic, acetic, propionic, butyric and pentanoic).

Concentration of the products formed at this stage depends on the hydrogen partial pressure. Low partial pressure corresponds to a higher production of acetic acid [20].

Acetogenesis.

Products of acidogenesis will be converted by acetogenic bacteria into acetic acid (acetic acid anion), hydrogen, and carbon dioxide. Acetogenic bacteria are obligate syntrophs [1][17]. Hydrogen is released by their metabolism and is toxic for them. Therefore, there is a symbiosis between acetogenic bacteria with autotrophic[2] methane bacteria that use hydrogen (hydrogenotrophic). Syntroph bacteria and methanogenic archaea must live in very close proximity in flocks or biofilms to be able to transfer hydrogen, see Fig. 2.2

The free energy of reaction $\triangle G$ of the main acetogenesis reactions is positive (see Tab. 2.1) implying that the reaction is only possible with the addition of energy. This energy is supplied by the methanogenesis reactions thus forming a symbiosis. Syntroph bacteria and methanogenic archaea prosper at the limit of thermodynamically possible energy gain[19]. For this reason they grow comparatively slowly and cannot easily adapt to sudden changes. Their activity can be reduced by sudden increases in the loading rate, feedstock, pH and temperature fluctuations, for example.

[1] They must act together with bacteria in a different trophic group to digest a substrate

[2] An organism that produces complex organic compounds (such as carbohydrates, fats, and proteins) from simple substances present in its surrounding

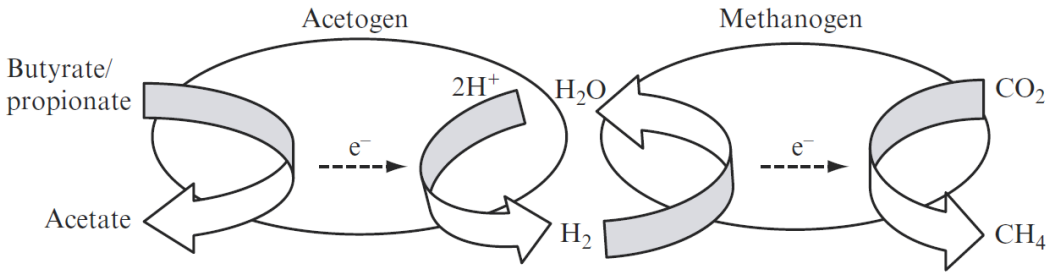

Figure 2.2.: Interspecies hydrogen transfer. Source [25].

Table 2.1.: Example of acetogenesis reaction. Conversion reaction from alcohol to acetic acid. $\triangle G^o$ is the change of the free energy at standard conditions

$$CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + H^+ + 2H_2 \quad \triangle G^o = +9.6kJ/mol$$

The Gibbs energy of the above alcohol reaction can be negative when the temperature is increased (thermophilic) or pH is reduced allowing acetogenic bacteria to complete the reaction with a minimum energy gain.

Hydrogen is a key parameter to determine the stability of the biological process because high concentrations inhibit acetogens, thus hindering the transformation of long chain volatile fatty acids, decreasing pH and impeding methane formation. Increased concentrations of hydrogen or volatile fatty acids (VFA) give an indication of an instability in the process.

In this step, two trophic groups of bacteria are also present. These are homoacetogenic bacteria, which reduce hydrogen levels producing acetic acid and syntrophic acetate oxidizing bacteria that work in the opposite direction.

Methanogenesis.

In this last step, acetic acid, hydrogen and carbon dioxide are converted by methanogenic archae into carbon dioxide, water and methane. This group of archaea is divided in two subgroups: hydrogenotrophic (hydrogen consumers) and aceticlastic (acetic acid consumers).

Table 2.2.: Standard free energy of main methanogenic reactions

Hydrogenotrophic archaea	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	$\triangle G^o = -131,0kJ/mol$
Aceticlastic archaea	$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$	$\triangle G^o = -35,9kJ/mol$

The Gibbs free energy of both methanogenesis pathways are negative which indicates

that both can provide energy to the acetogenic bacteria, see Tab. 2.1. Methanogens have a higher affinity to hydrogen than to acetates.

During anaerobic agricultural digestion, methane production at plants with a large Organic Loading Rate (2.5 - 3$kg\,oDM/(m^3 \cdot day)$) is dominated by hydrogenotrophic archaea with an important presence of syntrophic acetate oxidizing bacteria [19]. Furthermore, [26] found a mixture of hydrogenotrophic bacteria and acetoclastic archaea in three parallel digester feeds with energy crops operating at an OLR of $3.5kg\,oDM/(m^3 \cdot day)$. On the other hand, at plants with a low OLR and in waste water treatment plants methane production is dominated by aceticlastic archaea.

Other reactions

Gas quality is affected when sulfur rich feedstock is processed at a biogas plant. Sulphur is transformed into hydrogen sulphide H_2S by reducing bacteria. The resultant increase in H_2S causes corrosion within the engine which powers the generators and consumes hydrogen that is essential for methanogenic archaea function.

Hydrogen sulfide is reduced to elementary sulphur by aerobic bacteria through an oxidative reaction termed biological desulphurization; the sulphur is then carried by the digestates which increases the fertilizer value. This aerobic reaction is made possible by the addition of air to the gas storage (3.5- 4,5% of the gas production)[20]. The drawback of this is that elementary sulfur can serve as a initial material for H_2S production, decreasing the overall efficiency of biological desulphurisation[27].

Another method to reduce H_2S is by adding iron salts. The iron salts bind to H_2S to form solid iron sulphide while still within the liquid phase. Iron sulphide is then removed with the digestates.

2.1.3. Nutrients

In addition to nutrient groups (carbohydrates, proteins, and fats), microbial microorganisms must also be provided with vitamins, enzyme, hormones and minerals (macronutrients and trace elements) that they do not produce on their own but are essential to their normal function. A balanced ratio of the different macronutrients and micronutrients is important for efficient fermentation.

Macronutrients.

Microorganisms are composed on average of 50% carbon, 11 % nitrogen, 2% phosphor, and 1% sulfur. These elements must be provided for an efficient process. The quantity of a single nutrient is not as important as the ratio between the concentrations. The recommended $C/N/P$ ratios in digesters are between 100:5:1 and 200:5:1[18]. The optimum C/N ratio for anaerobic digestion is defined as between 20 and 70 depending on the substrate characteristics [28, 29].

Trace elements.

Trace elements or micronutrients are those of which the average concentration is lower than $50mg$ per kg of biomass. Required elements are cobalt (Co), nickel (Ni), (Mo), (Se) and iron (Fe). Some bacteria require zinc (Zn), copper (Cu) and manganese (Mn).

The required quantities are specific to the respective populations and are difficult to determine because of the vast variety cultures and their adaptability. Low trace elements concentrations may inhibit enzyme production and thereby interfere with the metabolism of the methanogens. Fermenting bacteria are not affected by this deficiency of trace elements which leads to an accumulation of VFA . If the acids content exceeds the buffer capacity of the digestates, it can cause a destabilization of the biogas process [30]. In [31] it was found that addition of trace elements effects methane production and microbial composition. In [32], a slowly decrease of trace elements deficit did not effect methane production but generates a shift within methanogenic community. The long term stability of the system could not be determined.

Trace elements react with H_2S to form poorly soluble metal sulfides that are not readily available to the methanogenic archaea [27, 30]. For this reason, it is important to reduce H_2S levels first before adding trace elements, to guarantee that they are available for the process.

Minimum concentrations of trace elements depend on the exposed organic load [33]. Reference concentrations used in the industry are $Ni > 0.3, Co > 0.12 - 0,16, Mo > 0.2$ and $Se > 0.01 - 0.02$ which are in good agreement with the trace elements requirements at the lower and middle organic rate.

	Organic Loading Rate		
Element mg/kg	Low	Middle	High
Ni	0.4	0.6	0.8
Co	1.2	1.6	2.2
Mo	0.4	0.45	0.5

Table 2.3.: Trace element minimum concentration and OLR. Adapted from [34]

2.1.4. Process parameters

The following parameters can be modified by feeding schedule and feedstock characteristics.

Ammonia inhibition

Ammonium nitrogen($NH_4 - N$) is produced by the biological degradation of nitrogenous matter [35]. In practice this mineralization percentage is estimated based on previous measurements in plants fed with similar substrates.

There are two principal forms of inorganic ammonia: Free ammonia NH_3 and Ammonium ion (NH_4^+). Both compounds are in an equilibrium that depends on the temperature and the pH of the solution[3]. Free ammonia is toxic for the microbial community, especially for the acetoclastic methanogens [35], but with time, methanogenic bacteria can adapt to higher ammonia concentrations [37].

Different concentrations of $NH_4 - N$ have been reported in literature to produce varying levels of inhibition in the process[4]. Concentrations lower than $5kg(NH_4 - N)/Mg$ are described as causing a modest inhibition [37]. Also, a concentration between 3 and $5kg(NH_4-N)/Mg$ can cause inhibition due to the dependence of pH, temperature and the adaptation of the substrates to a high ammonia concentration .

Hydraulic residence time (HRT)

HRT is the average residence time of the feedstock inside the digester. There is a large interest in the industry to reduce the residence time in order to reduce the investment cost, but a reactor operated with a short HRT causes methanogens to be washed out from the system. Maintaining a high residence time is important for a stable operation, better tolerance to toxicity, higher load and faster recovery [38].

Each substrate has its own degradation time[5]. The minimum hydraulic residence time ($MHRT$) can be described as the minimum residence time required by any of the feedstocks in the mixture that will be fed into the digester. The resulting residence time is dependent on the feedstock that requires the longest residence time and this can generate larger design volumes which make the investment of the biogas plant infeasible.

Another aspect to consider is the feedstock mixture in co-digestion plants. This is especially important to plants dealing with manure and energy crops. Short residence times (below 50 days) can only be achieved by biogas plants with a large percentage of manure $> 80\%$, while for biogas plants operating with 100% energy crops residence times of more than 100 days are required [39]. A typical residence time in biogas plants in Germany is between 60 and 90 days [40].

[3] At higher pH levels, the equilibrium moves towards ammonium ion and at a higher temperature towards free ammonia [36]

[4] Direct Calculation of (NH_3) is not often used in practice due to the difficulty of measurement[37].

[5] The degradation time of substrates rich in fats is much shorter than substrates containing carbohydrates.

Note: The work reported in this thesis focuses on wet fermentation, in which HRT is equal to Solid Retention Time (see sec. 2.1.5).

Organic loading rate (OLR)

The OLR defines the daily feeding rate of organic dry matter (oDM) per unit digester volume. Higher OLR requires a smaller reactor volume and lower capital cost. However, an increase in the OLR above a maximum sustainable organic loading rate ($MOLR$) would lead to higher hydrolysis bacterial activity rather than methanogenic bacterial activity. This effect would increase VFA, and cause an irreversible acidification[41].

Variation of the OLR has been used to shape microbial populations, allowing the digester to recover faster from stress periods and non-optimal conditions (see sec. 2.1.7).

Typical values for wet fermentation are between 2 to $4 kg\, oDM/(m^3 \cdot day)$ [42].

Dry matter (DM)

Inadequate mixing conditions hinder the efficient transfer of organic material to the active microbial biomass [43]. The DM value is used as a parameter to estimate the mixing conditions inside the digester even though they are dependent on the viscosity of the digestates. The reason is that the dry matter is simple to measure on site and is a well-known parameter used by the operators.

Digestate viscosity varies with the characteristics of the substrate mixture as shown in [44] where different feedstock mixtures with the same dry matter have different viscosities. The viscosity and the design of the mixing system [45] as well as the addition of supplements like enzymes can affect mixing conditions[46].

Wet fermentation reactors fed with energy crops and manure usually have dry matter content below 16% [43]. As an alternative to determining dry matter in the reactor content, it is possible to limit the maximum DM in the input material.

2.1.5. Type of reactors

There are different reactor configurations according to the substrate characteristics and design philosophy of different manufacturers (e.g., reactors treating waste water require a larger (SRT) than the hydraulic retention time to improve the amount of solids that are hydrolized). Tab. 2.4 comprises the classification criteria.

Table 2.4.: Classification criteria anaerobic reactors

Feeding	Fermentation steps	Temperature	Dry matter	Solid Residence Time (SRT)
Continuous Batch	1 step 2 step (Hydrolysis) more steps	Mesophilic Thermophilic	Wet fermentation Dry fermentation	SRT= HRT SRT>HRT

Adapted from [20]

Dry batch reactors

Reactors of this type are normally used with substrates of high dry matter content (30 - 40%). Feedstock is fed once and then inoculated with the leachate from a previous batch. This kind of reactor does not have mechanical agitation so the contact of the substrate with the microorganism is supported by the re-circulation of leachate. There are many alternative heating systems, the most common is to heat the leachate using an external heat exchanger. Electricity consumption is lower as its mainly used is for the leachate recirculation pump.

One of the main advantages of dry fermentation is that can it handle higher percentages of contaminants and, for that reason, is normally used to treat the organic fraction of municipal solid waste [47].

The main disadvantage of this system is that it requires the combination of many reactors in order to achieve a semicontinuous biogas production. Methane production per unit of feedstock is not maximized [17].

Dry continuous reactors

Dry continuous reactors are of the plug flow type. Feedstock enters the system at one end and flows through the reactor until reaches the other end, in this way different retention times are avoided. Dry fermentation systems allow for an OLR between 7 and $10 kg\, oDM/(m^3 \cdot day)$[20]. There are three main types[47]:

- Vertical tank: in which new feedstock is mixed with digestate and enters at the top of the tank. Due to its own weight, the material moves to the bottom where it is collected (e.g DRANCO process).
- Vertical tank with horizontal plug flow: In this case material is obliged to move horizontally in the vertical tank due to the separation baffle that covers 2/3 of the diameter. Pressurized biogas is injected at the bottom for agitation (e.g. Valorga process).
- Horizontal Tank: Feedstock enters at one end and is moved using a series of high capacity agitators to the other end. Kompogas, Thöni and similar processes

Fixed Bed Reactors

This kind of reactor is common in the treatment of waste water with low dry matter content but a with a high organic load. The SRT is longer than the average HRT keeping high concentrations of biomass in the reactor with a low treatment time.

As a part of flexible power generation, these kinds of systems are installed as the second step of an anaerobic digestion plant (acetogenic and methanogenic). Liquid input for the fest bed reactor can either be generated in a hydrolysis tank with a further separation[48] or from leachate produced in a leach bed (dry batch) reactor [49, 50]. The main advantage of this system is that the liquid fraction containing fast digestible dissolved organic compounds can be stored and when needed be sent to the fixed bed reactor generating a flexible gas production[48].

Microbial organisms are retained in the reactor through a packaging medium which prevents bacteria washout. This configuration supports high organic loads as well as periods of starvation / low or no load.

Continuous Stirred Tank Reactors (CSTR)

This reactor type normally operates with dry matter between 2 and 12%; however, this limit is only a guideline as the operation also depends on the feedstock viscosity in order to achieve reactor homogenization [51]. In these reactors HRT and SRT are the same. Due to the continuous stirring, the microbial organisms are not retained so there is a risk of bacteria washout. The minimum HRT time should be longer than the doubling time of both the syntroph bacteria and the methanogenic archaea (see sec. 2.1.4). Maximum OLR are between 2 and $4 kg\, oDM/(m^3 \cdot day)$[42].

One or two steps fermentation are possible depending on the feedstock and design philosophy. Mixing is one of the most important aspects in the design of the system. There are different configurations possible according to the feedstock characteristics and design[17]. Frequent and high-speed mixing regimes are detrimental for the process because the generated shear stress can destroy flocks or biofilms formed by the communities of syntroph bacteria and methanogenic archaea, which are required for hydrogen transfer [18] (see sec. 2.1.2).

CSTRs are the most common type of digester in agricultural plants in Germany and allow the treatment of both liquid and solid feedstocks [40, 22].

Tests and measurements developed in this work were done on this type of reactor.

2.1.6. Process stability

The efficient and stable operation of reactors relies on a relationship between fermenting bacteria, specialized acidogenic and acetogenic syntrophs, and methanogenic bacteria with diverse parallel pathways for substrate metabolism [52]. For energy

production, a microbial community must have a stable metabolic function over time, despite the perturbations that can occur in real life [53].

Stability of a system is commonly determined in two ways: performance indicators (pH, Chemical Oxygen Demand (COD) removal, VFA, ratio between VFA and Total inorganic Carbon (TIC)) and functional stability of the microbial community [54]. Common practice is to assess the stability of a system using performance indicators (see sec. 2.5.1) which can be measured in commercial plants.

Information about population characteristics is often not available as this requires trained personal and specialized equipment not usually available in biogas plants. A change of microbiome composition (i.e decreasing of methanogenic population) can be potentially used as an early indicator of process instability [55, 56]. The most widely used methods in determining microbiome of anaerobic digestions are denaturant gradient gel electrophoresis (DGGE), Fluorescent in situ hybridization (FISH), cloning of 16S rDNA, and Terminal restriction fragment length polymorphism (tRLFP). A review of these techniques can be found in [57, 56].

Functional stability does not imply community stability. A well performing digester at constant functional properties pH and COD can have an extremely dynamic community even at constant conditions [54]. In order to asses functional stability the following three ecological parameters must be involved [58, 53, 59].

Microbial community diversity (Richness)

The diversity of the microbial community gives an indication of the existence of parallel pathways for degradation of organic compounds and such diversity provides a more robust functionality over time [60, 61]. A minimum level of diversity in the microbial community is required to achieve functional stability [52, 62].

It is possible to have stable reactors with low diversity indexes. In this case, it is the flexibility of the community that ensures stable operation.

Evenness of microbial community structure (functional organization)

The evenness of the microbial community structure is determined by the distribution of dominant and resilient microorganisms. Low evenness implies that only a few of the many species are in dominant numbers. Intermediate evenness is characteristic for a robust system as the community has more capacity to use its varied array of metabolic pathways[53].

Decreases in microbial evenness can be used as a warning indicator [59].

Microbial community dynamics

The dynamics of the microbial community concerns the number of major species that on average come to significant dominance during a defined time. This varies because

shifts in the type of community present have been observed in both functionally stable and unstable reactors [59]

Population dynamics that keep functionality after a disturbance over time can be seen in three mechanisms [63].

- Resistance: The degree to which microbial composition remains unchanged in the face of a disturbance.
- Resilence: The rate at which microbial composition returns to its original composition after being disturbed.
- Redundancy: The ability of one microbial taxon to carry out a process at the same rate as another under the same environmental conditions.

2.1.7. Management strategies in anaerobic digestion

The microbial community in reactors can be shaped to enhance methane production, to improve resistance to high nitrogen levels or to operate at high organic loads.[59].

Management strategies can be divided into 1) microbial based strategies which directly affect microbial community and 2) operational based strategies which affect the community indirectly .

Microbial based strategies

- Inoculum: An acclimated microbial consortium with balanced nutrients that is used to accelerate the start up of the digestion process [64, 65, 66]. Reportedly three different sources of inoculum were able to gradually adapt and generate a functional microbial community to produce biogas from maize [67]. The inoculum from a plant processing maize silage enables a faster start up. Results indicate that the effect of inoculum is time limited.
- Bioaugmentation: The addition of a particular species or consortium of species could allow plant operators to change the existing microbial community to optimize processing of certain feedstocks or operation at defined conditions [68]. Bioaugmentation presents some technical issues such as bacteria strain isolation and maintaining the bacterial augmenter in the digester over time[69]. Successful bioaugmentation has been reported to modify the bacterial population to improve hydrolysis and acidogenisis, while few successful investigations reported the use of methanogens due to their high sensitivity to stress conditions [70].

Operational based strategies

- Feedstock modification keeping OLR constant: Substrate changes have been found to have no effect on VFA concentration but decrease the total alkalinity

[71]. Moreover, three reactors initially similar, attained a complete different microbial composition after being fed three different kinds of feedstock, showing that archaeal population is strongly influenced by feedstock composition [72]. Additionally, a comparison of 78 anaerobic digester samples, found that digester bacteria are clustered by feedstock type [73].

- Feeding schedule modification keeping OLR constant: In one study methane production and bacterial population of two different feeding scenarios were compared keeping the OLR constant. The first was a shock loading with 100 % glycerol and the second a gradual increase in glycerol until the same percentage. Different feeding approaches led to different bacterial population, both are functional for methane production [74]. Another study used three different feeding schedules comparing feeding every 2 hours, once a day and once every two days [75]. In both studies, an increase in VFA occurred after the less frequent feeding but returned to the normal levels before the next feeding [74, 75]. Furthermore, a higher biogas production was achieved after a feeding event in the less frequent schedule but the total biogas production did not increase [75, 76]. Variation in performance of lab reactors operated in parallel is attributed to inoculum heterogeneity and random factors that affect microbial community structure [76]. In contrast, two full-scale reactors operated as parallel reactors presented similar microbial communities [26]. Variations to microbial structure can also be explained by the different conditions generated in a lab reactor compared with full scale (ibid). All the studies conclude that, at the same OLR, changes in feeding intervals influence the bacterial community composition, while methanogenic communities remained stable. A high degree of functional stability was achieved while changing the feeding pattern, in spite of this alteration of evenness, dynamics and diversity of the bacterial community (see sec. 2.1.6). The process became more tolerant to high levels of ammonium and high organic loading rates [77, 75].
- Modification of OLR: An increase of the OLR from 2.11 to 4.25 $kg\,oDM/(m^3 \cdot day)$ was successful but was followed by an increase of VFA, which after a few weeks of adaptation returned to the original levels [78]. Additionally, an increase in the diversity of the bacterial communities was found as the result of an OLR increase. However, archaeal communities remained almost constant. The OLR was increased until the reactor failed by increasing VFA and decreasing buffer capacity [79]. In [69], faster acid processing was found after an initial OLR increase which induced a shift of the microbial community. These results show that tolerance to OLR variation can be built up in anaerobic digesters, and the response of digesters exposed to variations in OLR depends on past operation.
- Modification of HRT: In [80], it was demonstrated that variation of HRT and OLR can influence and even control the presence of single bacterial groups. However, digesters fed under the same conditions do not generate a unique community structure linked to the process parameters.

- Temperature modification: Temperature plays a major role in the microbial composition of the system (see sec. 2.1.1). In [81], the effects of a temperature increase from 32 to 52 °C were evaluated in an Upflow Anaerobic Sludge Blanket (UASB)[6]. They observed that a temperature increase drastically effects the microbial community and therefore operational performance. A higher performance was found at 37°C.
- Ammonia resistance: In [82], an increase in nitrogen levels changed the bacterial population, shifting it from the acetoclastic to the hydrogenotrophic methane pathway, which is well known to be more robust against ammonia toxicity. Improve microbial diversity makes it possible to process high nitrogen content substrates, however, this adaptation, which depends on the nitrogen level will not always be enough to avoid a process failure. Three bacteria clusters were identified as changing numbers according to total ammonia concentration and temperature [83]. Moreover, no significant differences in the methanogenic groups could be observed between these clusters [83]. The first cluster in this study was characterized by low nitrogen concentration, low free ammonia concentrations and more stable conditions (ibid).

2.2. Operational flexibility of electric power systems

The change in the energy mix according to the German Renewable Energy Act (2017) will be based on technologies with the lowest levelized cost of energy as is the case of wind and PV power. The high share of fluctuating energy sources and their uncertainties in power generation raise the requirements for operational flexibility of the power system to compensate for such fluctuations and supply the resulting residual load.

Operational flexibility is defined in [84] as "the technical ability of a power system unit to modulate electrical power feed-in to the grid and/or power outfeed from the grid over time". Five major kinds of actions can be identified to increase the flexibility of the power system [85].

1. increase in flexible power generation from renewable energy sources (mainly bio-energy) and conventional energy sources (natural gas and enhanced flexibility of coal power plants and CHP units)
2. use of power storage systems and increased sector coupling (power to gas, power to heat, power to mobility)[86].
3. demand side management [87, 88]
4. grid extension for interregional transport and balancing

[6]This kind of reactor is commonly used for the treatment of waste water. As a difference with the fixed bed reactor (see sec. 2.1.5), solids are fixed in a blanket of granular sludge which suspends in the tank.

5. improved integration of European electricity grids and markets through transnational transport and balancing

Apart from hydro power in which capacity is dependent on the local topographical conditions, bio-energy is the most mature option for renewable energy flexible power generation [89, 90]. However, bioelectricity generation remains more expensive than wind and PV due to the larger weight of the feedstock cost in generation cost and far fewer generating units. Although at the moment flexibility can be provided by fossils fuels, in the long term it must be provided by low carbon alternatives.

2.3. Flexible power generation in biogas

In Germany the Renewable Energy Sources Act (Erneuerbare-Energien-Gesetz, EEG) has, since 2000, promoted renewable energy technologies, like bioenergy, which would not be able to compete with conventional energy technologies under market conditions. Up to 2012 base-load oriented power concepts were promoted using fixed feed-in tariffs maximizing full load hours independent of demand and electricity prices. EEG 2012 required a change to flexible operation by promoting the increase of installed electrical capacity with the introduction of an optional market premium which made remuneration partially dependent on electricity prices in combination with a direct marketing and flexibility premium [85]. The plants participating in direct marketing can gain an additional source of income by providing system services such as control power in balancing markets.

In EEG 2014 direct marketing became mandatory for new biogas plants and they were required to double electrical installed capacity but only feed half of the capacity in any one year. Increased investment cost and the reduction of the electricity price caused by the withdrawal of the bonus for using energy crops which are the main substrate of 78.2% of the biogas plant in Germany [91], halted the development of new projects. Only small 75 kW plants based on manure are still being built. Flexibility premium continues until cover the financing cap of 1350 MW.

EEG 2017 introduced the use of tenders, as previous applicable for Wind and PV, for any new installation. The expansion of new biomass plants is limited to 150 MW per year from 2017 to 2019 while in the same period the limits for PV are 2500 MW, onshore wind 2800 and offshore wind 6000 MW per year. Important here is that existing plants can apply to participate in the tender process and in this way extend their operating contract by 10 years. As a condition they have to deliver regulated power, use a maximum of 50% energy crops and only half of the installed electrical power will be remunerated.

From August 1 2014 until December 31 2018, 900.4 MW additional biogas electrical capacity has been supported by the flexibility premium. The average electrical power of the plants before power increase was 485 kW and the average increase is 474 kW [92]. The expected balancing power generated by the flexibility premium is 2.73

GW. This value is obtained assuming the same electrical power increase and that 1350 MW will be financed.

The future of existing biogas plants in Germany depends on their ability to deliver flexible power as low carbon provider of grid services with a maximum ramp down and ramp up of 15 minutes [90].

Additional income available for electricity spot prices and balancing markets should cover the additional investment cost required for flexible operation. On the EPEX Spot SE market, the profitability of a demand oriented production strategy depends on average price levels and price variance. Both indicators have fallen in the recent years [85]. Price signals are also not clear for balancing market because wind and PV capacity have tripled from 2008 to 2015, while balancing markets reserves have been reduced by 15%, and cost by 50% [93]. The average balance power use weekly was also reduced from 216 MW in January 2009 to 83 MW in May 2017 [94].

Biogas plant flexibilization is currently one of the main challenges that needs to be overcome to ensure a complete integration of biogas plants into the energy supply system in the future [95]. The crucial components or process characteristics defining the flexibility of the process are [95]:

1. Type of substrate and substrate supply: Substrate characteristics that plays a major role is the degradation rate. Manure has a lower degradation rate than sugar beet. In this sense, if it is required to increase the biogas production to match an electricity peak, this can be done by a punctual addition of sugar beat which will generate a higher peak compared with manure even if both feedings have the same potential biogas production. Trace element and nitrogen content in the mixture also play a role. Even if a substrate does not have a high degradation, feed will be required which will guarantee the balance of nutrients to the microorganism. A further aspect is the capacity to store substrates like household organic wastes, which are difficult to store and should be processed as received. Energy crops can be easily stored as silage and made available when required.
2. Type of conversion process: Depending on the type of reactor (see sec. 2.1.5) their capacity to deliver flexible gas production varies. Fixed bed reactor can support a high organic load and survive for long periods without feeding but require feeding with a rapidly degradable fraction [96]. Most of the agricultural plants in Germany are CSTR reactors which cannot support high load variations. Trace elements requirements depend on the applied OLR [34, 33]. It has been observed that the capacity to support high variations of load can be build up according to the feeding used, see sec. 2.1.7
3. Gas storage capacity on site: Flexible power generation implies altering the power output of the plant. The degree of flexibility will depend, in the case of generation on site, on the installed electrical capacity and the available gas storage. Feeding on demand can help to extend the existing capacity by increasing gas production when gas is required and reducing when not. The

limit of this variation will depend on the substrate characteristics and kind of reactor. In [13] a reduction of the gas storage demand of 42% was achieved by the implementation of feeding on demand in a CSTR digester. [97] compared constant feeding and feeding on demand with an ADM1 model. The feeding on demand scenario enable a reduction of gas storage capacity also reducing the investment costs.

4. Type of biogas utilization: Biogas is mainly used for electricity generation. Production and generation are coupled using storage available on site. An important part of the income of existing plants is the sell of the excess heat produced. Flexible generation requires the installation of additional heat storage for which an individual evaluation of the heat profiles is needed to determine storage capacity and characteristics. If the gas is cleaned to biomethane and injected into the natural gas network, production and generation are separated, increasing flexibility.

Not only the capacity but also the speed of the shift are important to characterize the flexibility potential in biogas plants [90].

- short term flexibility (reaction time: 5 to 15 min, duration up to several hours) these implies engine shut down or a substantial decrease of its operational capacity, usually up to 1 h. The implementation only requires control technology for the CHP units.
- mid term flexibility (reaction time: $>$ 15 min, duration according to a weekly schedule). Duration of load alternation is longer than in short term flexibility. Change of load is triggered within a day, of for the next day. Implementation requires CHP overcapacity and enough gas storage. Flexibility can be improved by feeding on demand with corresponding control of the biological process. Heat storage may be required according to existing heat delivery contracts.
- long term flexibility (reaction time: per season, duration months) Reasons for such operation could include seasonal adjustments like: higher heat demand in winter, availability of the substrates and long periods of high production of wind or solar. Implementation requires the whole plant to match long term changes in the operation.

2.4. Anaerobic digestion models

Anaerobic digestion is a complex multistage dynamic process that includes the activity of several bacteria and archaea groups. How the composition of bacterial groups varies with changes in the feedstock, temperature, type of reactor and operating conditions is not well known [98]. The microbial community is considered unique in each digester mainly as a result of the operating conditions and substrates

composition [53, 99, 77, 73, 100, 26, 83]. In addition, highly dynamic communities are also present even when operating conditions and substrates are constant [101, 54, 102, 55, 103]. Due to high microbial community variability, developing an anaerobic digestion model depends on the objective to be achieved, for instance, process understanding, dynamic simulation, optimization or control[104].

Two different approaches have been developed.

1. "Black box" Models: This kind of model tries to mimic the system behavior, analyzing the correlation between input and output data based on site measurements using different data mining methods like artificial neural networks [105, 106], decision-tree controller[107], and Fuzzy logic [108, 109].
2. Dynamic Models: These models try to emulate the basic structure of the system and the relation between the different state variables, based on bacteria kinetic and stoichiometric assumptions. One of the most used is the Anaerobic Digestion Model 1 (ADM1) developed by the IWA Anaerobic Digestion Model Task Group [110]. An overview of the ADM1 adaptations and applications are presented in [111].

Dynamic models are not broadly used in practice due to the large number of parameters and the expensive, labor intensive experiments required to generate data for calibration and validation [112]. The monitoring systems and equipment required for efficient monitoring are not often available at biogas plants. Additionally, with a large-scale digester the condition of a completely mixed system cannot be guaranteed; however, ADM1 assumes perfect mixing [113]. A simplified version of the ADM1 Model was used by [13] to determine the feeding strategy for obtaining flexible biogas production and stable process conditions based on a model predictive controller.

Black box models are widely used with linear programming to maximize biogas production under defined conditions. Biogas yields are calculated using different methodologies based on feedstock composition in carbohydrates, lipids and proteins [114], or based on batch fermentation tests (BMP)[115]. A BMP has been widely used to describe biogas production under the assumption that it will be similar in large scale plants. The BMP of substrate mixtures have been fitted to polynomial equations [114] as well as exponential equations [116]. The aim of [116] was to optimize the feeding patterns and maximize the economic performance of the plant, considering a variety of OLRs.

In [11], linear programming was used to optimize the substrate blends by varying the HRT, anticipating that the expected biogas production at a specific HRT in the batch test would be like continuous operation at that HRT. Methane production was then calculated using estimated degraded COD (Chemical Oxygen Demand) from stoichiometric relation. Process stability was ensured by linear restrictions based on heuristic knowledge. This control strategy was validated using alkalinity ratios and methane potentials as diagnostic parameters in a m^3 digester [117].

A simplified model presented in [14] (IBA model) uses BMP to estimate the substrate biogas production curves in real conditions. The biogas production of a substrate mixture is defined as the addition of the biogas production curves of each substrate in the mixture. This approach offers better results in a laboratory digester, than some dynamic models like the ATB Model [118] and its calculational requirements are simpler.

One of the main advantages in using batch test is that the information about biodegradability of the different fractions and total biogas potential is used directly and is not derive from an equation as is the case of ADM1[119].

The main disadvantage here is that the conditions at which a BMP test is performed are not the same as in an operating digester and biogas yield curves may be different. Furthermore, digester conditions change with the feeding and operating conditions which may also affect the biogas yield curves (see sec. 2.1.7).

A biogas plant control based on the gas production obtained by the addition of the gas yield kinetics of single substrates has been patented [120]. Feeding quantities are generated based on the available substrates and the characterization of the digester conditions. This characterization is done, for example, by the gas production, digester temperature, acids concentration and pH measurements at different points in the digester.

2.5. Digester Monitoring

Currently the number of measurements is limited in most of the plants to one per day, which is enough to characterize a continuous digester feed, but insufficient for a biogas plant providing flexible power with feeding on demand. This kind of feeding will demand an online supervision of the biological process due to the continuous changes in feedstock quality and quantity. Modification in the feeding program can generate process imbalances that must be detected on time to avoid large disturbances on the biological process and possible economic loss.

2.5.1. Parameter and measurement principle for the sample analysis

Digester conditions are often characterized by chemical parameters [121]. Common online measurements are pH and redox potential [37], however sensors for this provide very limited insight into the dynamics of the microbiological process [122], and for that reason are not often used in practical applications.

The characterization of intermediate metabolites in an anaerobic digestion process is standard practice for the characterization of biological process stability [123, 37, 124].

The parameters most used to determine the stability of the anaerobic digestion process are total VFA, concentration of each specific acid (especially acetic and propionic), and alkalinity and hydrogen concentration in the liquid phase. Other parameters, like pH, are less sensitive to VFA concentration changes in a well buffered anaerobic digester [125].

Different measurement principles have been described [126, 122]. for online measurements of the biogas process. These include indirect, non-invasive measurements implying an elaborate calibration and interpretation such as the use of Raman spectroscopy [127, 128], Near Infrared Spectroscopy (NIRS) [129, 130] and Mid Infrared Spectroscopy (MIR) [131]. Dissolved hydrogen in the liquid phase has been successfully measured using an extractor located in the substrate providing an interphase between extraction gas and aqueous medium [132, 133]

Direct invasive measurements are an alternative which requires taking and preparing samples and then sending them to a measurement device. Titration is one of the most used methods to determine the VFA [134, 42] and the alkalinity ratio VFA/TIC (Total inorganic Carbon), in German literature the parameter is called FOS/TAC (Flüchtige Organische Säuren/ Total Anorganic Carbon) [135, 125]. VFA can also be estimated by spectrofluorimetry [136]. The measurement of individual VFA is normally done by chromatography such as HPLC (High Pressure liquid Chromatography), Gas Chromatography or GC Mass spectrometry [15, 133].

Following the (TOS) guidelines, NIRS has been successfully used to determine total VFA, individual volatile acids and dry matter. Representative sampling in this reference is obtained with a dedicated recirculation loop [129, 137, 138].

Of the analytical measurements, the most widely used in commercial power plants is the titrimetric determination of VFA/TIC ratio, because it is simple, inexpensive and robust. Calculating the VFA/TIC ratio is an empiric method and it is not standardized. The numerator indicates VFA accumulation and denominator indicates Total Inorganic Carbon (TIC) or buffer capacity. Buffer capacity measures the resistance to a pH change that can be generated by VFA accumulation.

Values less than 0.3 are considered indicative of as an indicator for a stable anaerobic process [37]. However values between 0.4 and 0.6 are still considered as characteristic for a stable system in agricultural biogas plants[133].

A problem with VFA/TIC analysis is that it does not provide an estimation of the individual fatty acids because they have a similar acid dissociation constant pK_a, see Fig. 2.3 on the following page. In digestate there are several compounds such as ammonia, sulphide, phosphate and high concentrations of bicarbonate which interfere with the VFA titration results [139].

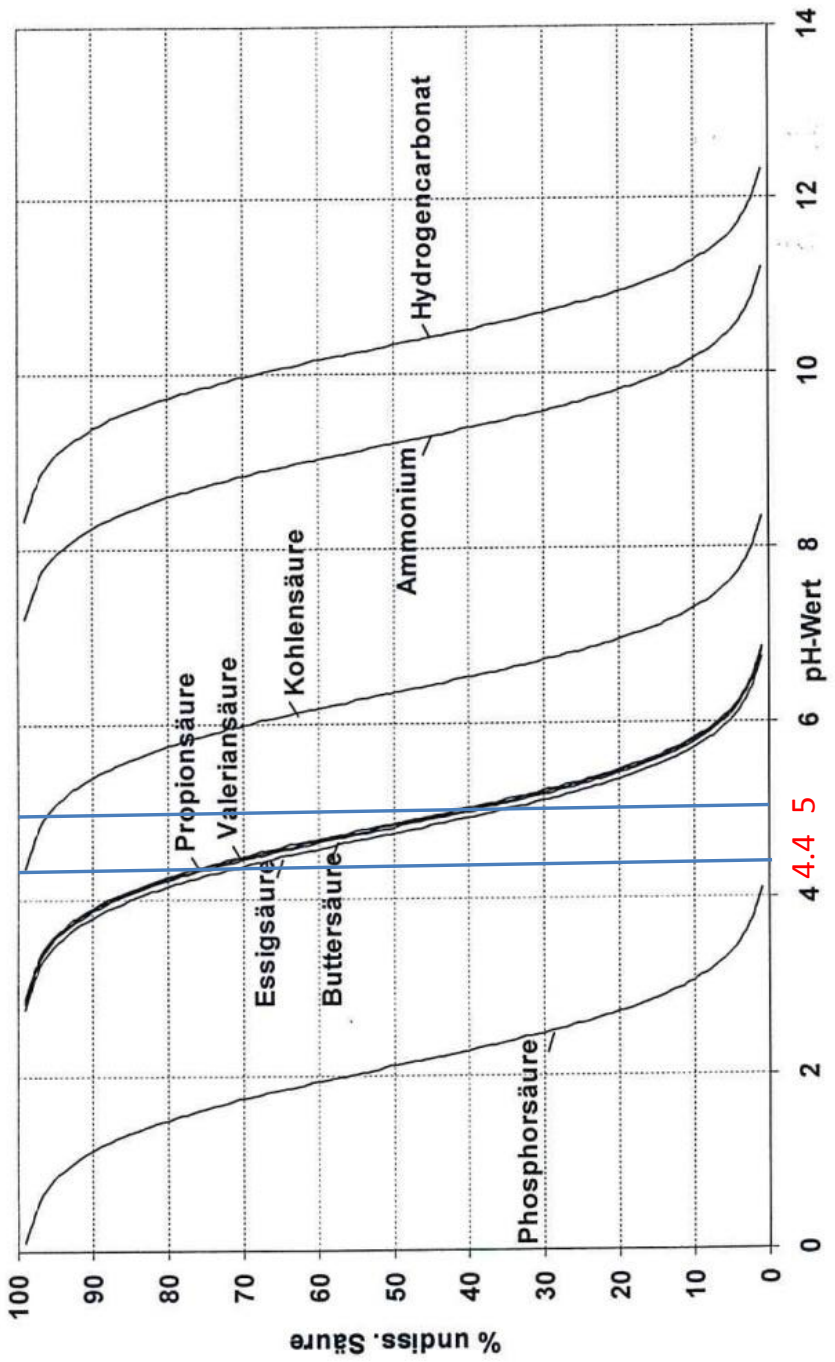

Figure 2.3.: Dissociation curves for weak acids and bases. Adapted from [140]. (English key: Phosphorsäure Phosphoric acid; Essigsäure Acetic acid; Buttersäure Butyric acid; Propionsäure Propionic acid; Valeriansäure Valeric acid; Kohlensäure Carbonic acid; Hydrogencarbonat Hydrogencarbonat; undiss. Säure undissociated acid; pH-Wert pH value)

Concentration of individual fatty acids provide more knowledge of process stability [15, 121, 141]. An increase in total VFA can be interpreted as organic overload or a kinetic uncoupling between acid producers and consumers which is typical in stress situations [123, 122]. In both cases actions should be taken to avoid a reactor failure. A stable system can, however, have high levels of VFA. For this reason it is important to consider relative changes and no single values [121].

A complicating issue is that the results depend on the sampling method and sample preparation. Samples should be filtered or centrifuged before analysis because titrant consumption increases with the solid contents generating a possible overestimation of the VFA [142]. In most commercial plants samples are simply filtered without defining a minimum particle size. The filtered sample still has a high heterogeneity which makes the results un-reproducible and dependent on the operator. For the titration itself, there are autotitrators on the market which avoid errors generated by manual titration.

Most autotitrators on the market use the direct titration of the sample from initial pH to two pH end points. Due to its simplicity and accuracy this procedure is also recommended by [139] when the composition of the sample is not known.

The TIC value is estimated by the amount of acid required to reach pH 5.0, $M_{pH=5}$ and VFA content by the additional acid required to reach pH 4.4, $M_{pH=5\,to\,4.4}$. Between starting pH and pH 5 buffer chemical substances like carbonate, phosphate and ammonium are present and a fraction of the VFA. Between pH 5.0 and pH 4.4, the VFA is mainly present with a fraction of the buffer chemical compounds [125].

$$TIC = \frac{20ml}{V\,[ml]} \bullet M_{pH=5} \bullet 250 \tag{2.1}$$

$$VFA = (\frac{20ml}{V\,[ml]} \bullet M_{pH=5\,to\,4.4} \bullet 1.6 - 0.15) \bullet 500 \tag{2.2}$$

$$\frac{VFA}{TIC} = \frac{M_{pH=5\,to\,4.4} \bullet 3.2}{M_{pH=5}} - \frac{0.3}{\frac{20ml}{V\,[ml]} \bullet M_{pH=5}} \tag{2.3}$$

2.5.2. Theory of sampling guidelines

The TOS guidelines describe seven unit sampling operations [143, 144] that must be followed in order to implement a correct sampling procedure. The sampling operations described here were used for the design of the sampling device in this project.

• *Operation 1 Transformation of lot dimensionality.* This step is necessary to transform a 3-dimensional digester, which is difficult to sample, into a 1-dimensional object. This is done by pumping the material through a pipe where the length of one dimension becomes much larger than the other two. If the pipe is connected back to the digester a re-circulation loop is generated. In principle all the contents of the digester will pass through the pipe, if the substrate is pumped often enough.

Taking a sample from a digester is equivalent to taking a cross section of the flow through the pipe. The main problem here is taking an exact cross section. In [145], it is proposed to take a sample with a side valve in a vertical up flow in which the substrate is flowing at high speed, generating a turbulent flow which implies a high degree of mixing, resulting in a homogeneous cross section. The sample taken with this procedure does not fully comply with TOS because the cross section of the pipe is not completely extracted (delimitation error) and the homogenization assumption cannot be verified. A proposed solution to this issue is the install of a dedicated re-circulation loop with a small pipe diameter and a low capacity pump [127].Then the sample is taken when a three way valve located at the vertical pipe is turned towards a side connection, and the volume is determined by the flow rate and time that the valve remains in the side position. In the case that there is more than one digester, each of them will require a separate re-circulation loop.

• *Operation 2 Characterization of 0-Dimenstional (0-D) sampling variation.* This should be used when there is no space correlation between the samples or when the correlation is not known. For this analysis it is not relevant whether the samples are taken continuously or discontinuously. The characterization is done by repetition of the sampling procedure and the calculation of the variance σ^2.

• *Operation 3 Characterization of 1-D (process) variation by variography.* In this case, there is a space correlation of the samples taken at consecutive intervals. A characterization is done with a variogram to detect the process variation frequency and is then used to modify the sampling frequency in order to avoid the risk of underestimating the process variation [143].

• *Operation 4 Homogenization by mixing or blending.* In order to reduce the heterogeneity it is important to agitate the digester before sampling. In every step of the sampling procedure each composite sample (defined as the addition of different subsamples or increments) should be well-mixed before being sent to the next step.

• *Operation 5 Composite sampling.* Due to the heterogeneous characteristics of the substrates it is necessary to generate a sample with as many increments (subsamples) as possible.

• *Operation 6 Particle size reduction.* The constitution heterogeneity of the substrate can only be achieved with a particle reduction or with comminution or filtration.

• *Operation 7 Representative mass-reduction.* A digester has a typical volume of $10^3 m^3$ and the sample required for the analytical measurement has a volume of

$10^{-6}m^3$. For that reason it is important that every mass reduction procedure performed follows TOS guidelines in order to be representative.

Procedures to generate the sample must be correct to obtain a representative sample. The sample itself cannot provide the information as to whether it is representative or not.

2.6. Gas storage system

Gas production is characterized by fluctuations and peaks [146]. Gas storage systems work as a buffer allowing decoupling of production and consumption. Due to this buffer volume, irregular consumption of a gas consuming unit or irregular production from a feeding on demand program can also be counterbalanced.

In the case of base load application, size of the gas storage and accuracy of volume measurements do not play an important role. Size of the gas storage is usually determined by the typical length of the maintenance schedule of the CHP unit or in many cases by the diameter of the required digester based on the feeding substrates[7]. In [22], it is recommended that gas volume should between one quarter to 2 times of the daily biogas production. Biogas volumes have been selected to vary depending on electricity use [147]. Co-generation units [8]should have a storage volume to cover the half of the daily production. A power station used to cover peak loads must be able to store the daily production of biogas.

The average storage capacity of biogas plants in Germany is 4.2 h the nominal engine consumption [91] with large variations between the different manufacturers.

For power on demand applications size of the gas storage depends on the shape of required load and type of feeding (continuous or feeding on demand). A higher accuracy in the gas volume level measurements is required. Volume levels are important to determine the capacity of the biogas plant to deliver the required load. They are also important to determine gas storage operating range in which gas level measurements are reliable and weather effects are minimized.

2.6.1. Types of gas storage.

Gas storage systems can be classified according to the operating pressure. Pressure limits vary, but in general can be classified in two categories

- Low pressure: An operating pressure between 0.5 to 30 mbars. Storages consist of membranes installed on digester tops or as an external storage. Most

[7]In the case of gas storage systems installed at the digester top.
[8]Engines at which the electricity and heat can be used as the same time

installed biogas holders (80 % [146]) are of this kind, and due to low operational and investment cost, almost all agricultural biogas holders are of this type. They can reach a volume up to 4000 m^3.

- Medium and higher pressure: Characterized by an operating pressure between 5 and 250 bar. In steel tanks or bottles. Volumes are relatively small, up to 100 m^3 at 10 bars and 1 m^3 at 250 bars. Investment and operating costs are high[22].

Low pressure gas storage systems can be classified according to number of membranes and support structure [148].

- Single Layer: Normally consisting of an EPDM membrane (ethylene propylene diene monomer) which has good UV resistance and elasticity. This is installed on top of a digester in which the volume is changing as well as the pressure. The storage is directly exposed to weather conditions (direct radiation) and because the membrane is not protected it can be mechanically damaged by external agents. Membranes should be always expanded in order to provide stability in rain and snow conditions, reducing the minimum operational volume. An external net is usually installed to limit the maximum expansion. A structure with insulation material is located between the membrane and the digestates surface to avoid contact between them and to insulate the digester. Stand alone single layer systems (pillows) are also an alternative to extend gas storage and because of their low pressure requirement, must be located at the end of a pressure cascade[148].
- Mechanically supported membrane: Is supported to avoid contact with the substrate. As with single membranes, volume and pressure vary. The retaining membrane is usually protected from weather conditions by an external membrane or a structure (concrete or metal tank). Gas volume determination is difficult as the membrane shape is designed for the maximum volume, so the volume is not well defined at lower gas storage levels. This kind of system can be installed on top of a digester or as external gas storage. When installed on top of a digester, substrate and gas storage membranes are separated by a net and insulation is provided by the air gap between two membranes.
- Air supported double layer storage. This system consists of two membranes often of a PVC textile. The internal membrane stores the gas and the external membrane protects the internal from weather conditions. The external membrane is supported by air that is pumped between the two membranes. The internal membrane moves up and down according to storage volume while the external is always extended and remains at the same position. Large gas storage volumes are possible. Gas volume determination presents the same issues as with a mechanically supported membrane as lower gas levels are harder to determine. This kind of membrane storage can be installed on top of a digester or as external gas storage. Insulation for the digester is given by the air layer between the two membranes. Biogas temperature is dependent on ambient

temperature as atmospheric air is pumped between both membranes. This system was patented in the 90´s [149] and is one of the most used in agricultural biogas plants. The main components of this system, when installed on top of a digester are presented in the following Fig. 2.4.

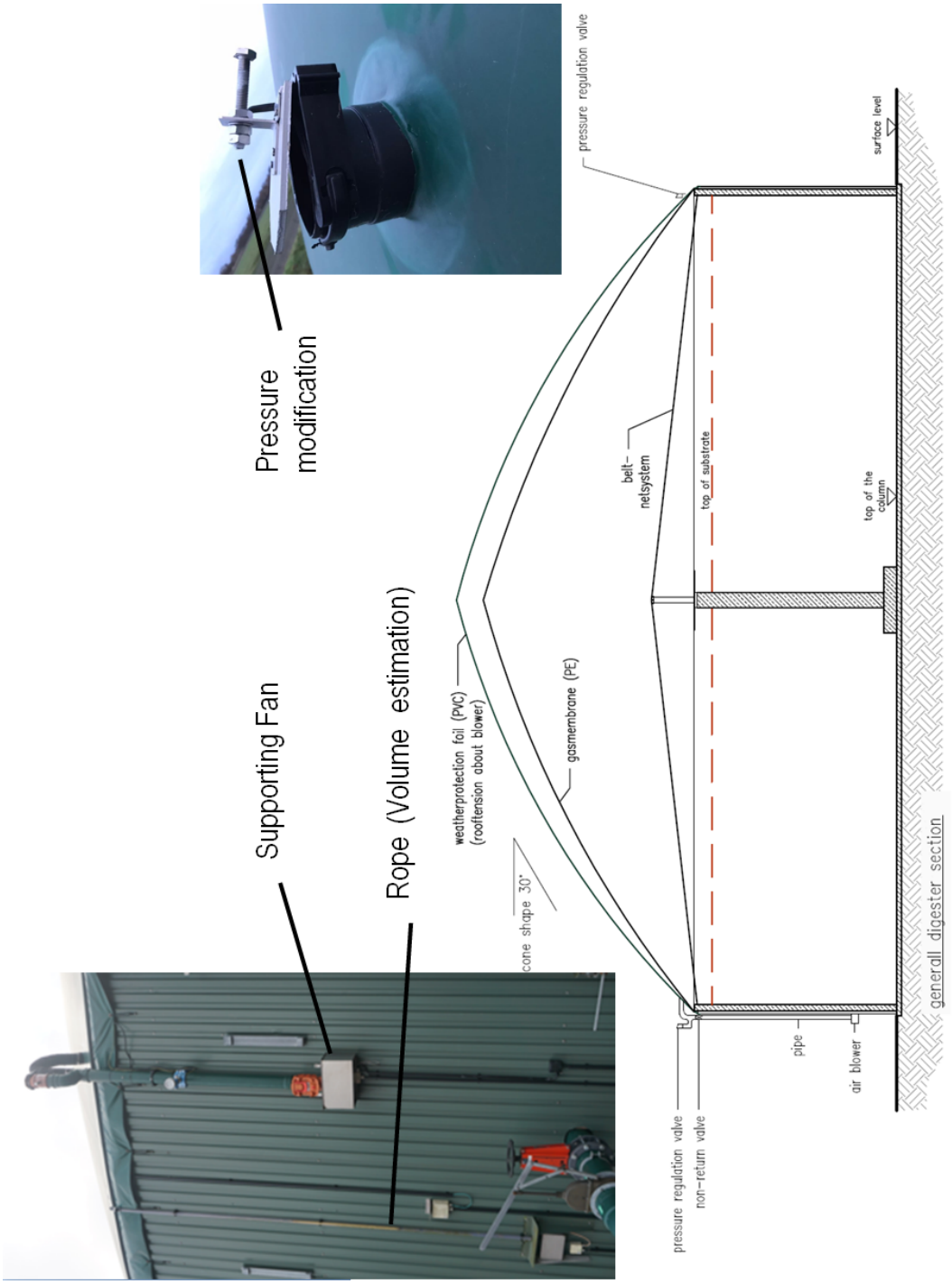

Figure 2.4.: Components air supported double layer gas storage

Operating pressure is relatively constant and determined by the pressure generated by the fan and the weight of the pressure regulation valve. The fan must compensate for gas volume changes and keep the external membrane continually extended to retain the stability of the system.

The work of this thesis will concentrate on air supported double layer storage because it is the most wide-spread systems (63% of the plants in Germany[91]) and has been found to be the most suitable for flexible power generation [148].

2.6.2. Measurements procedures

There are different alternatives to determine the fill level in an air supported double layer storage. Two measuring procedures are the most used in the market[150]:

- Water level gauge: Consists of a fixed hose filled with liquid located on the gas membrane surface, the height of which at the fixing point is determined by the hydrostatic pressure measured by a sensor at the lowest point of the pipe. The accuracy of volume measurements increases with multiple measurement points. In [151]a more accurate gas volume determination was obtained by installing three water level gauge sensors compared to a single rope system.
- Rope system: Consists of a rope fixed at one side, extended diametrically over the gas storage membrane to the other side of the digester. At the loose side of the rope a weight bar is installed, and the bar will move up and down according to the fill level of the membrane (see Fig. 2.4). The major drawback of the system is that the gas membrane does not have a defined shape and for that reason different gas volumes can generate the same measurements. On the other hand, this is the most common system installed in agricultural biogas plants which are running at full load where the accuracy of the system is not that important. This system is cheaper compared with a water gauge.

2.6.3. Gas Storage management.

In the case of multiple gas storages in a biogas plant it is necessary to ensure that all the gas storages have the potential to be used. Even though gas storages are connected by pipes the pressure and level of each gas storage is not the same.

The main reasons areas following:

- Different gas production in each of the tanks: An example of this would be a plant with a main gas production tank (digester) and a digestates tank where gas production is minimal, both with storage capacity. Gas production in the digestates tank depends on the HRT and the operating temperature [152].
- Size differences between gas storage units: Compared to digestate storage tanks, digester gas storage is usually smaller because they are sized based on

HRT and the digestates tanks are sized based on the number of months of required storage capacity.

- Pressure drops in gas lines: There is a pressure drop in the lines connecting gas storage units and for that reason, in order to move the gas, there must be a pressure difference between them.
- Radiation: Depending on the shape of the gas storage, different amounts of heat are transferred through radiation to the different gas storage units. Transferred energy per volume is higher for small gas storage than large gas storage[9]. A temperature increase will raise volume, generating imbalances in the system.
- Gas quality improvement: Biogas produced is saturated and its water content depends on gas temperature. Biogas must be dried to a low dewpoint to increase the efficiency of the engine and decrease both H_2S levels and operational costs. In order to decrease humidity several manufacturers have installed underground gas pipes to take advantage of the low and almost constant ground temperature to condense the water. H_2S reduction can be achieved by adding air in the gas storage. This reduction is made by aerobic bacteria, placed in a net inside the gas space. The area of this net is larger in the digestates storage tank which results in a larger reduction of sulfur in this tank. For that reason it is optimal to supply most of the produced gas in the plant from this tank. Because the digestates storage tank has a longer pipe distance to the engine in order to decrease water content, lengths of pipes from the different gas storages to the consumer are not the same, thus changing pressure differences and therefore the amount of gas provided by each storage.

For the above-mentioned reasons, it is necessary to implement a gas storage management system to maximize the use of the biogas plant.

There are two alternatives.

- Passive gas management. This schema generates a pressure cascade by adjusting the weight of the pressure regulation valves. A higher pressure is generated in the main gas producer (i.e. digester/s) and a lower pressure at the digestates storage. In normal operation gas level in digestates storage will be at maximum and the digester level varies according to production. The advantage is that no electrical equipment is required, and, for that reason, this is the most used system.
- Active gas management. The idea behind this is the same, but in this case there is an active control of the supporting fan or of the pressure regulation valves. Gas pressure is modified, and gas can be moved between the gas storages according to user requirements. Gas transport in a gas storage system

[9]In the case of air supported double layer systems installed on a top of a tank. The comparison is done calculating the ratio of volume to area. Radiation is directly proportional to the surface area.

was patented in 2009 [153]. Implementation of active gas management for flexible power production was reported in [154] by the research project MANBIO [155].

3. Methods

3.1. Commercial biogas plant description

Model implementation, online supervision of the biological process and gas storage management were implemented in a full-scale agricultural biogas plant, see Fig. 3.1 on the next page.

The biogas plant studied has an installed electrical capacity of $250kW$. The plant has been in operation since 2011 producing over 8600 h/year at full capacity. One of the reasons this plant was selected for this study was because the plant equipment and operation are run at a high standard and capacity.

Gas consumption is measured with a flow meter localized in the engine. Average consumption is $133m^3/h$ at 55% CH_4 at electrical power of $250kW$ giving an electrical efficiency of 34% which is considered too low. Unfortunately, the engine manufacturer had installed the flow meter in a different position and in a smaller pipe than the meter was originally calibrated for which biased subsequent measurements. Variations of up to 20% in the volume are possible based on the flow meter manufacturer. For this study, the engine will run at full capacity, the flow meter was not modified and the gas consumption will be taken as an indication.

The plant was fed with between 12 and 14 Mg of maize silage (varying with substrate DM) in ten feedings daily at 0, 4, 6, 8, 11, 13, 15, 17, 19 and 21 hours. Weather conditions also influence the rate of substrate consumption because the solid feeder is installed outside. On rainy days it was necessary to increase the feeding as water collected in the solid feeder and the feeding quantity is only controlled by its weight. Pig manure was fed once a day at 7.5 m^3. This quantity was fixed to achieve manure bonus.

The plant possessed one digester with a total volume of $1977m^3$ and one storage tank with a volume of $2761m^3$. The plant also had a central pump of $22kW$ with a nominal capacity of 90 m^3/h. The digester was equipped with two submersible agitators of $17kW$ and a paddle agitator of $15kW$, the storage tank had three submersible agitators of $17kW$. Gas storage capacity was 774 m^3 in the digester and 1264 m^3 in the storage tank, connected with a PVC pipe with an internal diameter of 186 mm.

The biogas storage capacity of the analyzed plant is about 60% of the daily produced biogas, a value larger than the average gas storage capacity of the majority of biogas plants in Germany, which is only 17.5% [91].

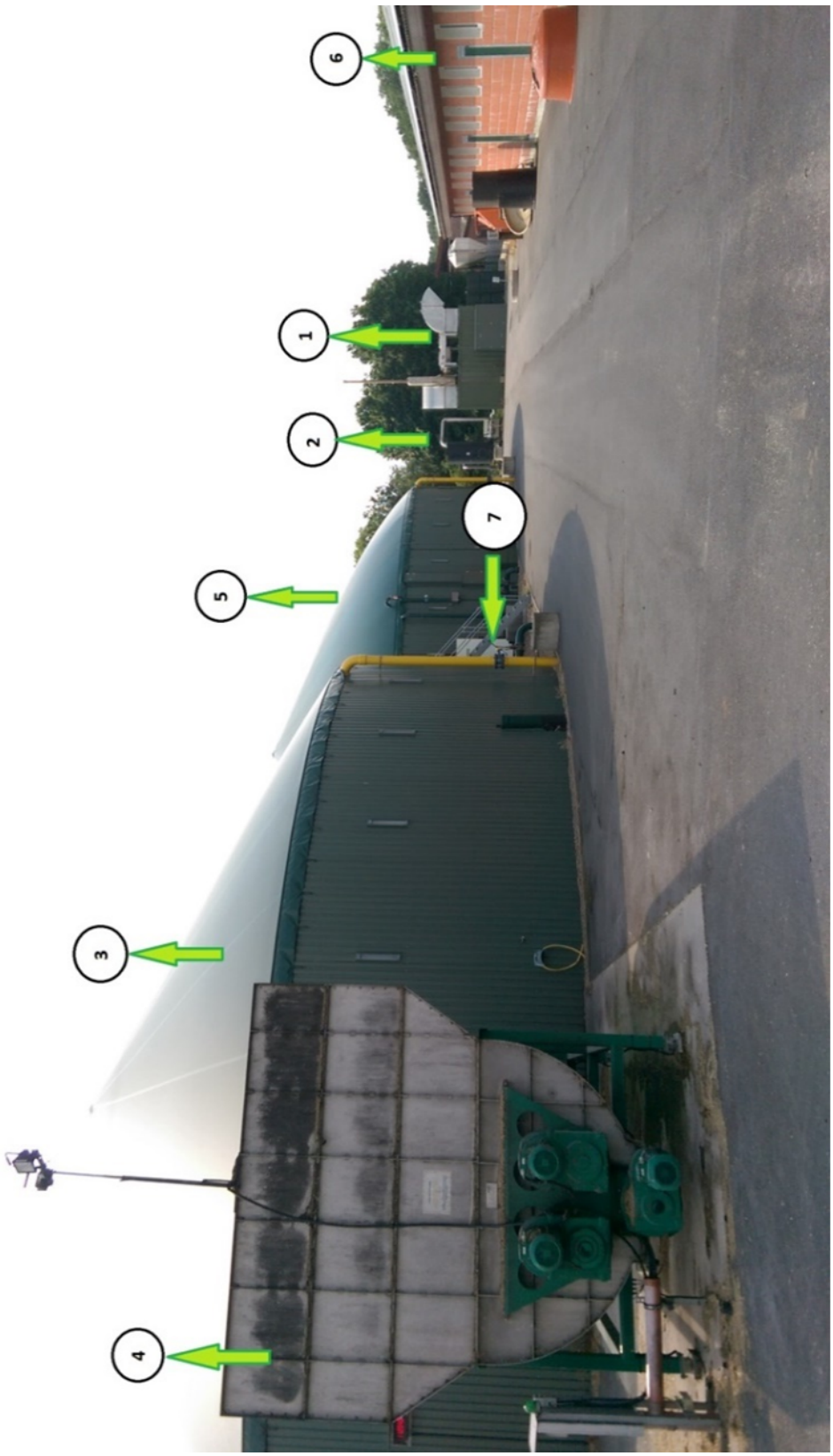

Figure 3.1.: Test plant

Feedstocks were intermittently analyzed, finding large differences (Tab. A.1). Dry matter values varied between 27.1 % to 39.9% which implied a variation of gas production of more than 60 m^3 biogas per ton. By multiplying the difference in the amount of biogas produced per ton by the daily feeding in tons (12 x 60 = 720 m^3) it is clear that the differences in gas storage requirements are within the range of the gas storage of the digester. Variations are due to the poor quality of the sampling method as material was stored in a silage plate exposed to weather conditions and by the different characteristics of the substrate depending its location on the silage plate; similar results were found in [156].

In addition the plant owner had different maize plants varieties in his fields in order to minimize the risk of a poor harvest. This is a normal practice in the region.

3.2. Model Description

Using the principle outlined in sec. 2.4 for the calculation of biogas production [14, 120], an optimization algorithm was developed with the objective to obtain a feedstock feeding schedule whose biogas production follows a required load. This algorithm minimizes the required gas storage capacity, while keeping operational parameters within a desired range.

A system operating in a certain range of process parameters will be stable and under these conditions the response of the system to a feeding event will be similar.

There are two main conditions under this assumption:

- Microbial community is functional stable (see sec. 2.1.6). VFA/TIC that was automated for this research study along and includes a representative sampling procedure (see sec. 3.4).
- Microbial population is resistant, resilient and functionally redundant between species in the variation range of the process parameters. It has been described in (sec. 2.1.7) how a microbial community can be shaped with operational based strategies to improve resistance against non-optimal conditions or to enhance methane production. Modification of the microbial community is achieved when extreme operation conditions are imposed on the system. In this study operation conditions are fixed in order to avoid extremes, within an operating range based on a heuristic knowledge. Microbial population may change by larger variations because the quantities in the resultant feeding schedule are not evenly distributed over the time. It has been found that these will increase tolerance to high ammonium levels and decrease the recovery time after high OLR [77]. If variation of operation conditions modifies microbial populations, generating changes in the biogas production, the new response of the system should be measured and then can be used as a standard response. The model is then updated to include the modification of the microbial community.

Synergetic effects may arise from the contribution of additional alkalinity, trace elements, nutrients, enzymes or any other additive which a substrate itself may lack [157]. In [158] a series of BMP test shows that synergetic effects are present in combination of co-substrates and that this effects were linked to the mitigation of inhibitory compounds.

Under the assumption that the imposed heuristic restrictions contribute that the substrates mixture does not generate a lack of nutrients, no synergetic effects are considered[1]. In [159] a series of degradation tests showed that individual substrates do not influence each other in their degradation kinetics in a stable system.

3.2.1. Biogas yield curves

A central part of the model is the determination of the step response or biogas yield curve to a feeding event. Three criteria were imposed to determine the step response of the system

- Similar reaction times as found in the full-scale digester.
- Generation of the step response in conditions like the digester
- As microbial population change with the feeding program and this may change the step response of the system. The method should include the possibility to update the step response over time.

In [14] this was determined using BMP to estimate biogas yield dynamics in real conditions. Gas yields measured in this way (VDI 4630) do not fit the criteria because a full-scale digester is continually fed and this test is for batch conditions. Biogas yield is usually measured only once a day which is not suitable for the determination of a feeding schedule because of high variations in biogas production.

An activity test (AT) [160] provides continuous gas volume measurements of a batch reactor. This test produces high data density (only limited by the measurement intervals i.e every 15 min). One disadvantage of this is that the methane content cannot be measured, therefore for analysis, it is assumed that methane content remains constant and its value is provided by a batch test. Additionally, in a batch test with a small volume the conditions of an operating digester with continuous feeding, agitation regime and temperature control cannot be reproduced. An AT provides a qualitative estimation of anaerobic degradation speed of a feedstock, which depends on the microbiological activity of the inoculum, itself dependent on the medium conditions.

Fig. 3.2, presents the biogas yield curve of maize silage and Corn Cob Mix (CCM) measured in an AT. Measurements are presented from the beginning of the test

[1] A continuous monitoring of the biological process is required to determine if there is a substrate deficiency, in particular in the case of trace elements which are not considered in the heuristic restrictions.

including the heating phase. It can be observed that for both series the production peak occurs at about 30 hours after test start. This can be explained by the composition: while maize silage is the whole maize ear including the cobs, the grains and occasionally the husks and portions of the stalks, CCM consist of grain and cobs only. The concentration of readily biodegradable fractions is higher in CCM than in maize silage. After the main peak the yield curves increase slightly showing the time that the bacteria require to digest the least biodegradable fraction.

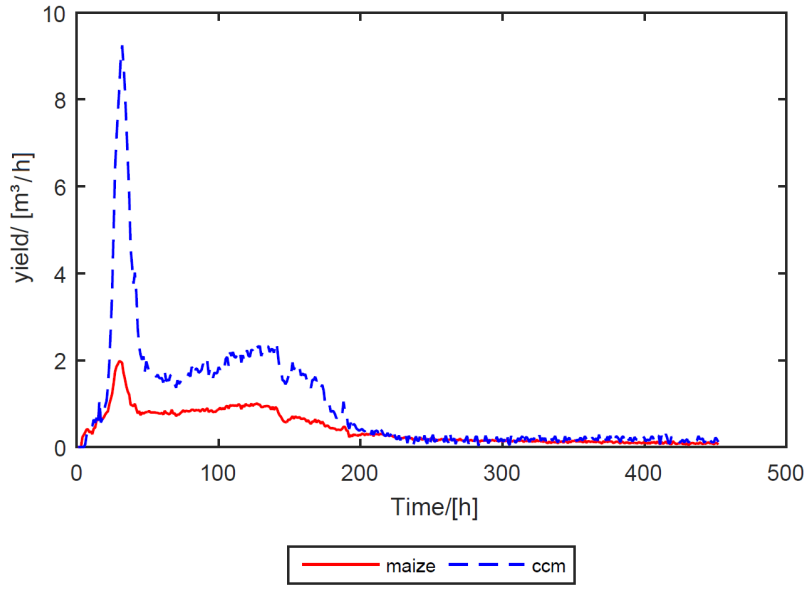

Figure 3.2.: Hourly biogas yield curve of CCM (dashed line) and maize silage (continuous line). Source: unpublished lab test. Ganagin, W. at HAWK

It was observed in [12, 13, 161] that system response after a feeding event is in the first 30 min, and large percentage of the biogas production occurs in the first 12 hours. The differences between reaction times can be explained by the different conditions between an AT reactor and an industry digester as follows: the influence of the inoculum (origin and degree of degradation), substrate preparation before the feeding (particle size reduction and homogenization), degree of agitation, temperature control (temperature fluctuation between collection, transport, test preparation and time to achieve the operating temperature) and adaptation and population changes within the microbial population [162].

Within a batch reactor, the substrates, microorganisms, enzymes and intermediate products are accumulated in the system whereas continuous feeding reactors are characterized by dynamic changes due to periodic substrate feeding and product removal [157].

Improvements to the model´s predictions can be achieved when the biogas yield curves are taken from a reactor with similar conditions to an operating digester

[11]. For that reason, is necessary to define the main difficulties in simulating these conditions in a laboratory reactor.

Physical conditions: Temperature can be easily maintained in the laboratory. On the other hand, homogeneity (quality of agitation), dry matter, shearing forces, viscosity, particle size distribution, surface/volume ratio are difficult to guarantee due to scale differences. In [163], after comparing seven waste water treatment reactors a linear relationship was found between bacterial richness, evenness (see sec. 2.1.6) and reactor size. A possible explanation for this is that larger reactors have more niche space available, therefore it becomes more likely that a small number of bacteria become dominant. This aspect requires a critical verification in order to transfer the results from lab scale studies to full scale [26].

Biological conditions: Are also difficult to guarantee due to the complex characterization of the bacterial population and its activity [164]. In order to guarantee similar biological conditions, the inoculum is taken from an operating biogas plant fed with similar substrates. However, the biological conditions of a digester can change depending on the substrate, and operational conditions [73, 53] and even with constant operational conditions and substrate feeding, bacteria populations can be highly dynamic [77, 101, 102, 55, 83, 76].

Despite the limitations of a biogas lab reactor the following setup was used to measure biogas yield curves of selected feedstocks.

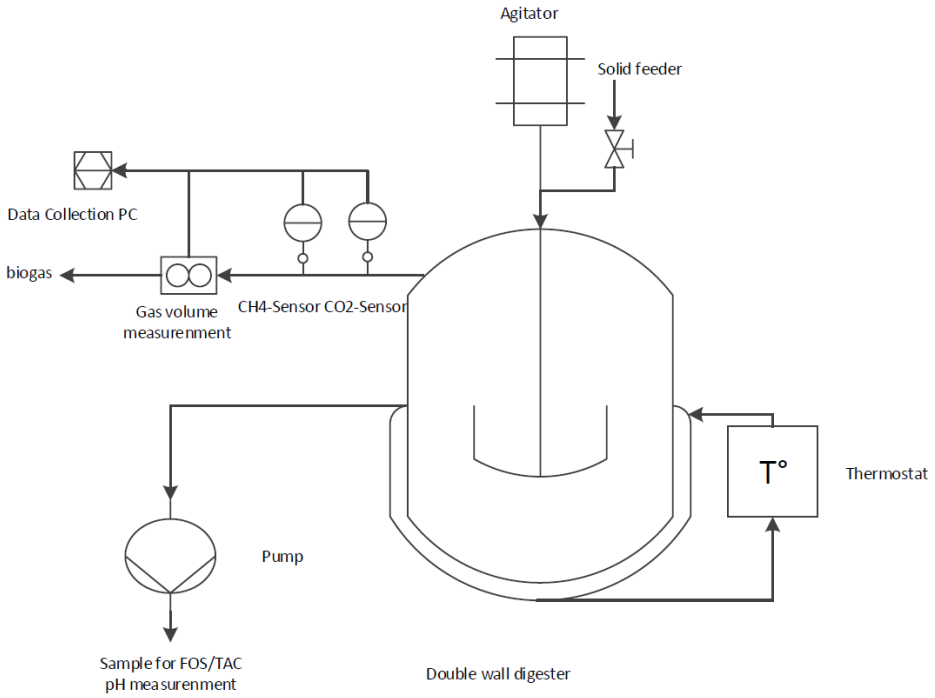

Figure 3.3.: Experimental setup continuous feeding lab reactor. Setup developed in Hochschule Emden/Leer

It consists of a double wall gas reactor with an internal volume of 10.8 l and is equipped with an vertical agitator that operates 5 min every hour. Operating temperature is mesophilic (40°C) and adjusted by pumping hot water through the outside chamber.

Gas production is continuously measured with a RITTER MilliGascounter MGC-1 1,19 ml and CH_4 and CO_2 concentration were measured with BlueSens sensors (BCSCH4 and BCSCO2 respectively).

Stability of the system was determined by the measurement of VFA/TIC and pH with a HACH LANGE biogas titration manager. A sample was taken after the agitation period. It was necessary to pump out about 500 ml of digestate to guarantee a fresh sample from the digester. Unused material was returned to the digester. During sampling and feeding time the digester was open, registered in the dataloger as periods of no production.

The inoculum for the fermentation was obtained from the commercial biogas plant described in sec. 3.1. Inoculum must be filtered to get a maximum particle size of 2 mm in order to avoid blockage in the pump in the experimental setup.

Maize silage and pig manure were stored in a cooling chamber at 4°C. Maize silage was chopped to $<$ 2mm. Pig manure was filtered before entering the digester. The characteristics of the substrates are presented in Tab. A.1 .

Three different sets of measurements were developed to determine the step response of maize silage, see Tab. 4.1. The first two correspond to single feedings with different OLR in order to determine whether the step response changes with OLR.

The purpose of the third was to determine whether it is possible to reproduce the biogas production measurements of a continuous feeding schedule. In this case, using two feedings a day and adding step responses of single feedings as obtained in the first two sets of measurements. If this is not possible it will be necessary to generate the step response with an exponential fit.

There are different equations that can be used to generate the shape of the step response. One study proposed an exponential fit to match the disintegration curve generated in the ORGA test [165]. Others [114, 119, 116, 166] try to fit the BMP curves also with an exponential fit as well. All the previous authors try to fit batch tests and validate the results with a continuous feeding digester.

The proposed approach is to fit biogas yield curves directly from measurements of a continuous feeding digester. Equation 3.1 is a possible candidate for the exponential fit that must be validated in a lab-simulated continuous feeding digester. HP can be estimated based on the height of gas production peak after a feeding, t_{peak} is the time between feeding and peak gas production. c is fitted to determine the curve that generates the total biogas production measured in a batch test. t_{max} is the duration of the batch test. The first two parameters can be estimated directly from the measurements of the biogas plant and may change according to the digester´s

conditions. The last two parameters are substrate dependent and should not change.

$$f(t) = \begin{cases} \frac{HP \cdot t}{t_{peak}} & 0 < t < t_{peak} \\ HP \cdot e^{-c \cdot t} & t_{peak} \leq t < t_{max} \end{cases} \tag{3.1}$$

Manure step response was also determined using the same lab setup.

3.2.2. Definition of the optimization problem

An optimum is found when the sum of the square of the differences between the equivalent energy generated by the biogas production and the required energy to deliver the load reaches a minimum that fulfills the constraints.

The optimization problem is a least-squares-optimization with constraints described in equation 3.2.

$$min \sum_{t} ||P \cdot x - d|| \; with \begin{Bmatrix} A \cdot x \leq b, \\ Aeq \cdot x = beq \\ lb \leq x \leq ub \end{Bmatrix} \tag{3.2}$$

The optimization will be applied in the range $[1, t]$, modifying the quantities of m different substrates and the time that these substrates are fed into the digester.

The components of the objective function are presented in the following equations:

Q_j is the vector with the quantities of substrate j $[1, m]$in Mg for the optimization interval t.

$$Q_j = \begin{bmatrix} x_{j,1} \\ . \\ . \\ x_{j,t} \end{bmatrix}$$

For the calculation of the objective function a new vector x with dimensions $[m \cdot t, 1]$ is used.

$$x = \begin{bmatrix} Q_1 \\ . \\ . \\ Q_m \end{bmatrix} = \begin{bmatrix} x_{1,1} \\ . \\ . \\ x_{1,t} \\ ... \\ x_{m,1} \\ . \\ .x_{m,t} \end{bmatrix} \tag{3.3}$$

The biogas yield of the substrate j, $g_{j,t}$ at a time t, is calculated as the difference between two measurements of the accumulated biogas production. The distance between the measurements $\triangle t$, determines the time scale of the biogas yield curve.

The biogas yield curve from the j substrate, S_j, is represented with the following equation 3.4. $L_j$is time series length of the substrate biogas yield curve.

$$S_j = \begin{bmatrix} g_{j,1} \\ g_{j,2} \\ . \\ . \\ g_{j,Lj} \end{bmatrix} \tag{3.4}$$

The energy production curve from the j substrate,E_j is calculated

$$E_j = \begin{bmatrix} g_{j,1} \\ g_{j,2} \\ . \\ . \\ g_{j,L_j} \end{bmatrix} \cdot \begin{bmatrix} M_j \\ M_j \\ . \\ . \\ M_j \end{bmatrix} = \begin{bmatrix} e_{j,1} \\ e_{j,2} \\ . \\ . \\ e_{j,L_j} \end{bmatrix} \tag{3.5}$$

For equation 3.5 the average methane content M_j was selected. [2].

Energy generated GE_i by substrates fed in the optimization interval $[1, t]$ at the time i is calculated with the following equation.

$$GE_i = \sum_{j=1}^{m} (x_{j,1}.e_{j,i} + x_{j,2}.e_{j,i-1} + ... + x_{j,i}.e_{j,1}) \tag{3.6}$$

$$where\ e_{j,i} = 0,\ if\ i > L_{j,} or\ i < 1$$

Equation 3.6 is simplified and transformed into matrix product $GE = P \cdot x$, arranging the terms of Matrix $P\ [t, m \cdot t]$.

d is the vector with the required energy. This vector is calculated based on the required load RL divided by engine efficiency at that load level[3], minus the energy generated from the feedings prior to the optimization interval pGE. This is calculated adding the energy yield curves (biogas yield curves multiplied by methane content) of substrates fed in the interval $[-\infty, 0]$.

$$d_i = RL_i/CHPef - pGE_i \tag{3.7}$$

[2]It is known that the methane concentration changes during the fermentation process. The main methane variation will be at the beginning of the biogas yield. Should this information be available it can be considered in equation 3.5

[3]electrical energy conversion efficiency can be found on the engine data sheet

3.2.3. Constraints

Stability and process parameters considered for the anaerobic digestion process are expressed as constraints in the optimization problem. The selected constraints are

- Ammonia inhibition
- Hydraulic retention time (HRT)
- Organic Loading Rate (OLR)
- Maximum Dry Matter (DM)
- Minimum C/N

Other restrictions can be imposed like:

- Price (Price): Price of the feeding substrates in the optimized feeding program should not be more expensive than the original feeding.
- Minimum substrate quantity: Operating restriction imposed to process a minimum quantity of substrate. For example manure to obtain the manure bonus.
- Gas storage range: Restriction of the maximum and minimum allowed gas storage levels.
- Total Energy: The total energy generated in the optimization interval must be the same amount as the energy required to satisfy the load profile.

These constraints are presented in Matrices A and Aeq with the limits b and beq. Matrices and vectors are generated by the vertical concatenation of the matrix´s correspondent to the different constraints. Matrix and vectors required for the practical implementation are presented in the Appendix.

$$A = \begin{bmatrix} AN \\ AHRT \\ ADM \\ AOLR \\ -AOLR \\ ACN \\ Vprice \\ AGS \\ -AGS \end{bmatrix} \quad b = \begin{bmatrix} bN \\ bHRT \\ bDM \\ bMaxOLR \\ -bMinOLR \\ bCN \\ bpriceorg \\ bGSMax \\ -bGSMin \end{bmatrix} \tag{3.8}$$

$$Aeq = \begin{bmatrix} ATE \\ AMS \end{bmatrix} \quad beq = \begin{bmatrix} bTE \\ bMS \end{bmatrix}$$

The following notation is used to specify the constraints based on the substrate properties.

- Dry mater dm_j
- Organic dry matter odm_j
- Nitrogen concentration n_j
- Carbon content c_j

Ammonia Inhibition

For a description see sec. 2.1.4. In practical applications and working at mesophilic temperature many plants are designed to work with a concentration below $4kg(NH_4-N)/Mg$[4].

Using this value as a reference and a mineralization level of 68%[5], the Maximum Allowed Nitrogen MAN in the input substrate mixture is:

$$MAN = \frac{4kg(NH_4 - N)/Mg}{0.68kg(NH_4 - N)/kgN} \cong 6kgN/Mg$$

This limit is defined by the daily input. For the calculation, however, the limit must be extended to the scale in which the feeding is developed.

Nitrogen fed in an interval i from m different substrates is defined by the following equation.

$$N_i = \sum_{j=1}^{m} x_{j,i} \cdot n_j$$

In the case that the feeding is considered every hour, the average nitrogen in 24 hours TN_i has been taken into consideration as substrate feed in the last 23 hours plus the nitrogen fed in the actual feeding.

$$TN_i = \frac{\sum_{j=1,l=i-24}^{m,i} x_{j,l} \cdot n_j}{\sum_{j=1,l=i-24}^{m,i} x_{j,l}} \tag{3.9}$$

For all the intervals $TN_i \leq MAN$. After replacing the terms in equation 3.9, the following equation is obtained.

[4]bwe Energiesysteme GmbH & Co. KG

[5]Average of many analyses in different bwe Energiesysteme GmbH & Co. KG biogas plants.

$$\sum_{j=1,l=i-24}^{m,i} x_{j,l} \cdot n_j \leq MAN \cdot \sum_{j=1,l=i-24}^{m,i} x_{j,l}$$

$$\sum_{j=1,l=i-24}^{m,i} x_{j,l} \cdot (n_j - MAN) \leq 0 \tag{3.10}$$

Equation 3.10 is valid for any feeding. The optimization considers that the last feeding was at time 0 and the new feeding program starts at position one. Based on that, for the first 23 feedings to be optimized it is necessary to consider the amounts of nitrogen introduced into the plant before the optimization period. This consideration must also be done for the other constraints.

Equation 3.10 should therefore be modified to be in the form $AN \cdot x \leq bN$ in order to be included in the optimization problem.

Hydraulic residence time

The aim of this restriction is to give the substrates the possibility to be completely degraded before leaving the digester. This restriction is important for two reasons: to minimize the economic loss of substrate leaving the system with a high biogas potential and to minimize the environmental issues of methane being produced outside of the digester.

For a description see sec. 2.1.4. In this analysis a minimum residence time $MHRT$ of 60 days has been chosen[6].

As in the last restriction, the HRT is defined for a day and is calculated by addition of the hourly feeds in these 24 hours, if the feeding schedule is every hour.

Quantities of m different substrates fed in an interval i is defined by the following equation.

$$X_i = \sum_{j=1}^{m} x_{j,i}$$

The residence time HRT_i considers substrate fed in the last 23 hours plus the quantity fed in the actual feeding. For the calculation it is assumed that substrate

[6]Residence time must be chosen based on the specific substrate mixture

density is equal to 1 which approximately corresponds to the fermented substrate. *digestervol* is the volume of digestates in the digester in m^3.

$$HRT_i = \frac{digestervol}{\sum_{j=1,l=i-24}^{m,i} x_{j,l}} \tag{3.11}$$

For all intervals $HRT_i \geq MHRT$. After replacing the terms on equation 3.11 the following equation is obtained.

$$\sum_{j=1,l=i-24}^{m,i} x_{j,l} \leq \frac{digestervol}{MHRT} \tag{3.12}$$

In order to include the HRT restriction in the optimization problem the equation 3.12 should be modified to $AHRT \cdot x \leq bHRT$.

Dry matter

For a description see sec. 2.1.4. A limitation of the maximum input dry matter D_{ref} was chosen to guarantee a uniform substrate DM input. This can be explained by the following example: A biogas plant operator wants to modify the plant operation from constant to flexible operation. At the beginning of the change, the dry matter inside the digester is low. For that reason and as the restriction is only given on the dry matter inside the digester, the algorithm suggests feeding mainly a substrate with a high dry matter (high energy density). This will result in an increase of the dry matter in the digester after time. Once the operator detects this situation, he must restrict the algorithm to change to substrates with low dry matter thus avoiding mechanical problems in the pumps and agitators. This substrate limitation will reduce the capacity to deliver power on demand.

A maximum input dry matter D_{ref} of 270 kg of solids in a Mg of substrate was selected based on the experience of bwe Energiesysteme GmbH & Co. KG. with plants operating on energy crops and manure. If the substrate mixture includes other kind of organic wastes this value should be modified.

As in the previous restrictions the DM is defined for a day and it must be extended to the feeding scale

Dry matter quantities of m different substrates fed in the interval i is defined by the following equation.

$$DM_i = \sum_{j=1}^{m} x_{j,i} \cdot dm_j$$

The average dry matter ADM_i considers substrate fed in the last 23 hours plus the quantity of dry matter substrates fed in the actual feeding.

$$ADM_i = \frac{\sum_{j=1,l=i-24}^{m,i} x_{j,l} \cdot dm_j}{\sum_{j=1,l=i-24}^{m,i} x_{j,l}} \tag{3.13}$$

For all intervals $ADM_i \leq D_{ref}$.

After replacing the terms on equation 3.17 the following equation is obtained.

$$\sum_{j=1,l=i-24}^{m,i} x_{j,l} \cdot dm_j \leq D_{ref} \cdot \sum_{j=1,l=i-24}^{m,i} x_{j,l}$$

$$\sum_{j=1,l=i-24}^{m,i} x_{j,l} \cdot (dm_j - D_{ref}) \leq 0 \tag{3.14}$$

In order to include it in the optimization problem the equation 3.14 should be modified to $ADM \cdot x \leq bDM$.

Organic loading rate

For a detailed description see sec. 2.1.4. For this calculation $4kg\,oDM/(m^3 \cdot day)$ was used as a maximum organic loading rate $MaxOLR$. A minimum limit is also selected to avoid large feeding variations, 2 $kg\,oDM/(m^3 \cdot day)$ was used as a minimum limit $MinOLR$.

As in the previous constraints, the OLR must be extended to the feeding scale.

Quantities of m different substrates organic dry matter fed in the interval i is defined by the following equation.

$$O_i = \sum_{j=1}^{m} x_{j,i} \cdot odm_j$$

The organic loading rate OLR_i considers substrate fed in the last 23 hours plus the quantity of organic substrates fed in the actual feeding.

$$OLR_i = \frac{\sum_{j=1,l=i-24}^{m,i} x_{j,l} \cdot odm_j}{digestervol} \tag{3.15}$$

For all intervals $OLR_i \leq MaxOLR$. After replacing the terms on equation 3.15 the following equation is obtained.

$$\sum_{j=1,l=i-24}^{m,i} x_{j,l} \cdot odm_j \leq MaxOLR \cdot digestervol \tag{3.16}$$

In order to include it in the optimization problem equation 3.16 should be modified to $AOLR \cdot x \leq bMaxOLR$. For the $MinOLR$ the equation is analog to 3.16 but multiplied by -1.

C/N Ratio

For a description see sec. 2.1.3. For this analysis the C/N reference, $C/Nref$ is defined as 25. Carbon quantities of m different substrates fed in the interval i is defined by the following equation.

$$C_i = \sum_{j=1}^{m} x_{j,i} \cdot c_j$$

where feeding is considered every hour, the average C/N ratio in 24 hours C/N_i must consider substrate fed in the last 23 hours plus the quantity of nitrogen and carbon substrates fed in the actual feeding.

$$C/N_i = \frac{\sum_{j=1,l=i-24}^{m,i} x_{j,l} \cdot c_j}{\sum_{j=1,l=i-24}^{m,i} x_{j,l} \cdot n_j} \tag{3.17}$$

For all intervals $C/N_i \geq C/Nref$.

After replacing the terms on 3.17 the following equation is obtained

$$\sum_{j=1,l=i-24}^{m,i} x_{j,l} \cdot c_j \geq CNref \cdot \sum_{j=1,l=i-24}^{m,i} x_{j,l} \cdot n_j \tag{3.18}$$

In order to include it in the optimization problem the equation 3.18 should be modified to $ACN \cdot x \leq bCN$.

Gas storage range

If the biogas plant is required to deliver network services like positive or negative reserve, it is necessary to guarantee that plant operation is restricted to a certain range of the gas storage capacity to allow delivery of the services. For example, in the case of negative minute reserve the operation range will be fixed at a lower level, so in the case that the network operator requires a shut-down of the generator the plant has several hours of storage capacity which will avoid flaring. Similarly, for positive reserve the plant will operate at a high gas storage level allowing the engine to run at full capacity when required by the network operator.

The total gas volume at the time i, GS_i is the addition of the gas volumes at standard conditions $VN_{k,i}$ of k tanks belonging to the biogas plant at time i. In case of the test plant with one digester and one digestates storage k is equal to D and S

$$GS_i = \sum^{k} VN_{k,i} \tag{3.19}$$

GS_i can also be calculated based on the gas consumption and production until time i. In order to calculate the gas storage GS_i at time i, it is necessary to identify main components like:

- Initial gas storage volume GS_0.
- Gas production in previous feedings: Corresponds to the biogas generated by the substrates feed in the interval $[-\infty, 0]$.
- Engine gas consumption : Gas consumption depends on the engine electrical efficiency at the required load level and resultant gas storage methane content. In order to calculate biogas volume consumed by the engine the calculation was simplified assuming a methane value in the stored gas equal to the last value before the optimization, M_0. This assumption was based on the observation that the methane level does not change much over time unless there is an imbalance in the biological process.
- Gas production for substrates fed in the optimization interval. This expression involves the optimization variables x (substrate quantities). Previous components are considered constant.

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The difference between the second and third component can be calculated using the previous defined d in equation 3.7 divided by the methane content.

To calculate the gas storage level GS_i it is necessary to consider the accumulated gas production in the interval $[0, i]$.

$$GS_i = GS_0 - \sum_{l=1}^{i} d_l/M_0 + \sum_{j=1}^{m}(x_{j,1}.\sum_{l=1}^{i} g_{j,l} + x_{j,2}.\sum_{l=1}^{i-1} g_{j,l} + ... + x_{j,i}.g_{j,1}) \tag{3.20}$$

$$where\ g_{j,i} = 0,\ if\ i > L_{j,}i < 1$$

Gas storage level GS_i is at standard conditions and without the humidity correction due to its temperature [148], which means that it cannot be directly measured in the plant. In order to be used in practical application it is necessary to calculate the total measured gas volume TVM, by multiplying the gas storage level using GS_i by a correction factor that depends on its pressure and temperature $CF(T,P)_i$. Both values change over time and must be estimated for the optimization interval t. The estimation of the correction factor over the time is presented in section 3.20, equation 3.28.

Corrected volume must be in the range of the max and min allowed gas storage $MaxS$, and $MinS$, respectively.

$$MaxS \geq GS_i \cdot CF(T,P)_i = TVM_i \tag{3.21}$$

$$MinS \leq GS_i \cdot CF(T,P)_i$$

After replacing the term on 3.21 the following equation is obtained.

$$\sum_{j=1}^{m}(x_{j,1}.\sum_{l=1}^{i} g_{j,l} + x_{j,2}.\sum_{l=1}^{i-1} g_{j,l} + ... + x_{j,i}.g_{j,1}) \leq \frac{MaxS}{CF(T,P)_i} - GS_0 + \sum_{l=1}^{i} d_l/M_0$$

$$where\ \frac{MaxS}{CF(T,P)_i} - GS_0 + \sum_{l=1}^{i} d_l/M_0 = 0,\ if\ \frac{MaxS}{CF(T,P)_i} - GS_0 + \sum_{l=1}^{i} d_l/M_0 < 0$$

The last condition is required especially at the beginning of the optimization interval to allow the transition of an initial gas storage volume GS_0 higher than the maximum gas storage level $MaxS$.

In order to include it in the optimization problem the equation should be modified to $AGS \cdot x \leq bGSMax$.

An analog equation for the minimum limit can be obtained. In this case it is necessary to multiply both terms by -1 and replace $MaxS$ by $MinS$ (minimum gas storage level).

Total energy

In order to compare the results of the different feeding programs, it is necessary that the energy generated by the substrates in the optimization interval $[1, t]$ is the same as the amount of energy to cover the load required in this interval.

The energy generated by the substrates is the sum of two quantities: The energy produced from previous feedings in the optimization interval (which is constant) and the energy generated by the substrates fed in the same interval.

The last term is calculated as the energy addition of every single feeding from the moment when the substrate is fed until the end of the optimization interval. There are two possibilities depending of the length of the energy production curve:

- Length of energy production curve $L_j < t$. In this case the substrates fed between $[1, t - L_i]$ will be completely degraded and the energy generated is $\sum_{k=1}^{L_j} e_{j,k}$, The substrates fed between $[t - L_j + 1, t]$ will be partially degraded and the energy generated $\sum_{k=1}^{t-i} e_{j,k}$ will be less as the feeding point is getting closer to the end of the optimization interval t.
- Length of energy production curve $L_j > t$. In this case all the times that the substrate j is fed in the optimization interval $[1, t]$ this will be partially degraded and energy generated is $\sum_{k=1}^{t-i+1} e_{j,k}$

The optimization problem should be in the form $ATE \cdot x = bTE$. The vector ATE considers only the energy generated by the substrates fed in the optimization interval.

bTE is a scalar and can be calculated directly as the difference from the sum of the required load electrical power, divided by the engine efficiency (to obtain the energy in the gas) minus the total energy produced from previous feedings in the optimization interval t which, as it was already mention, is constant.

Minimum substrate quantity

One common operational restriction is that a specific substrate quantity must be fed every day. A typical example is that there is contract with a waste supplier to process a substrate or, as in the case of previous German feeding tariff, there was the obligation that at least 30% of the volume fed per day should be manure in order to get a manure bonus.

3.2.4. Maximum and minimum substrate quantities.

Substrate bonds are defined as follows:

- Lower bound lb. For all substrates this limit is 0.

- Upper bound *ub*. Here it is necessary to make a distinction between solids and liquids. The maximum amount of solids is limited by the characteristics of the solid feeder system; in liquids by pump capacity.

3.2.5. Feeding adjustment.

Feeding can be adjusted at any time running the model again and updating the initial gas storage volume GS_0 and initial methane content gas storage M_0 which are model parameters.

Additionally, in the event that the biogas yield curve from the j substrate, S_j, has changed due to a variation of the operating conditions or it is expected to be different i.e after a weekend without feeding in order to reduce the gas production to the minimum due to the low electricity price. A new biogas yield curve for the j substrate, NS_j, can be measured or estimated based on digester gas production and updated in the model.

3.3. Model Validation

In order to validate the model the first step is to determine biogas yield curves of the substrate fed into the biogas plant. At the time of the measurements the only substrates available were maize silage and pig manure. In sec. 3.2.1 the benefits of measuring step response of the system directly in the plant instead of a lab reactor are discussed.

The original feeding program of maize silage was modified from feeding almost every 2 hours to every 12 hours, selected based on the findings in sec. 3.2.1 where most of the gas yield dynamics were found in the first 12 hours.

Longer feeding intervals were not selected for the following reasons:

- Decrease risk of organic shock
- A large variation of the gas compositions increasing CO_2 and decreasing CH_4 was noticed in single feedings (see Fig. 4.2). This variation is smaller in a feeding every 12 hours (see Fig. 4.3).
- Based on the yearly average electricity prices from the Day Ahead Auction of the EPEX SPOT SE[7] it was noted that the prices had two peaks which could be fitted with two feedings per day, so that step response calibration can also be used to simulate a feeding on demand scenario.

[7]The EPEX SPOT operates short term trading for Power in Germany, France, Austria and Switzerland

Pig manure step response was determined with from lab measurements, due to its low biogas yield (between 15 and 30 m^3/Mg) large quantities are required to generate a measurable effect. Increasing pig manure feed was also not desired by the plant owner because of increased digestate disposal cost. The manure feeding schedule was kept without change at 8am 7.5 m^3.

The feeding program for maize silage was selected to be at 9 am and 9 pm, with step response measured from the 9 pm feeding in which the pig manure effect is lower.

Continuous monitoring by the online system enables detection of possible system instability and timely reaction to this.

3.4. Sampling system experimental setup design

Following the guidelines of sampling theory (see sec. 2.5.2), a sampling device was developed, installed and tested in a commercial biogas plant.

The pump manifold is in PVC with an internal diameter of $150mm$. The sampling device was connected at an up-flow pipe located at the pressure side of the pump manifold. A sketch of the device is given in the following diagram. This sampling device is under patent [167].

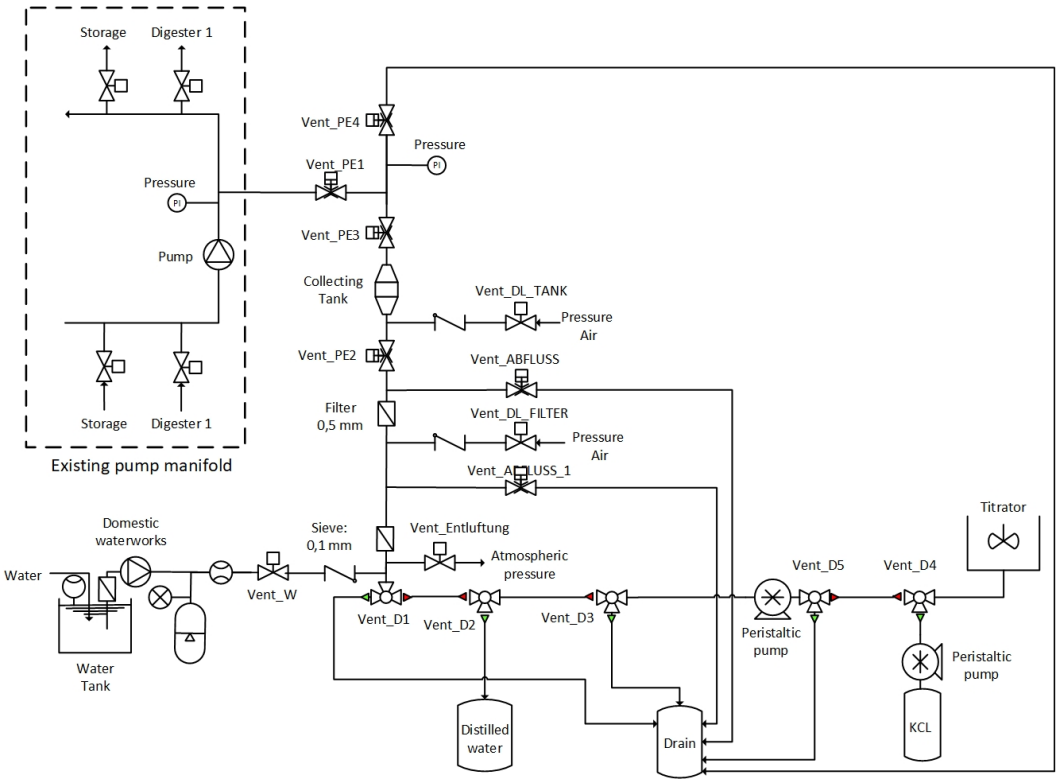


Figure 3.4.: Process diagram sampling device.

The circulation loop required to reduce digester dimensionality is generated at the existing pump manifold (*Operation 1*), see section sec. 2.5.2. At the manifold each tank has a connection at both suction and pressure sides of the pump, see Fig. 3.4. This configuration generates a circulation when the substrate is pumped from the digester to a tank, which can be the same digester. The advantage is that all the digesters connected to the pump manifold can be sampled, requiring no additional investment, and the sample can be taken while substrate is being pumped as a part of the normal operation without generating any additional cost or work to the operator.

It was decided to take subsamples from a side valve located at an up-flow vertical pipe even though a well-mixed cross section cannot be assumed, given a Reynolds number $Re = \frac{\nu \cdot L \cdot \rho}{\eta} = 66.68 \pm 4.65$, within in the characteristic range of laminar flow. This number was calculated based on the characteristics of the pump manifold and type of substrates fermented in the plant. The speed $\nu = 1.46 \frac{m}{s} \pm 0.04$ was calculated based on the nominal capacity of the pump, pipe diameter as a characteristic dimension $L = 0.147m \pm 0.002$, digestates density at 40°C of a plant fed with maize silage of $\rho = 1021.67 \frac{kg}{m^3} \pm 1.75$ and dynamic viscosity $\eta = 3.288 \frac{kg}{m*s} \pm 0.206$ based on the apparent viscosity at a shear rate of $\dot{\gamma} = 8.05 \frac{1}{s}$ [168].

In a side valve it is not possible to take a definite substrate cross section and, due to the flow characteristics, there could be a heterogeneous horizontal distribution in the pipe. An alternative to a side valve would have been to install a three-way valve at the pump manifold [138]; but due to the high capacity of the pump, the valve could have been easily damaged, causing a high risk of spillage, and for those reasons was not selected.

In Fig. 3.4, side valve *Vent_PE1* was installed as near as possible to the vertical pipe to reduce the risk that substrate from previous samples gets trapped, generating an error in the next sample. The sample point is located at the center of the vertical up-flow pipe. Before any sample is taken, the pump will operate for a certain time to purge the system and guarantee a fresh sample from the digester. The sampling process is divided into the following steps:

• *Step 1 Dosing sample:* From n equal digestates volumes a defined subsample volume $V_{subsample}$ is extracted (*Operation 7*). Subsample volume is determined by the air volume between three valves. A side valve connected to the up-flow pipe *Vent_PE1*, a bottom valve connected to a collecting tank *Vent_PE3*, and a top valve connected to a drain at atmospheric pressure *Vent_PE4,* see Fig. 3.4. At the beginning of the sampling procedure the air captured between the three valves is at atmospheric pressure and all the valves are closed. While substrate is pumped through the up-flow pipe, the valve *Vent_PE1* is opened and due to its higher pressure, material flows into the fix volume, compressing the captured air until its pressure is the same as in the pipe. At this time no more substrate can enter the sampling unit, and the *Vent_PE1* is closed. The sample volume is defined by the pressure in the pipe, which is fixed and depends on the pumping system, atmospheric

pressure (considered constant at the sampling time) and the air volume captured that can be varied according to the requirements of the sampling procedure, see Fig. 3.5 and Fig. 3.6 on the following page.

Subsample volume can be calculated with equation 3.22, where $V_{trapped}$ is the volume inside the valves *Vent_PE3, Vent_PE1* and *Vent_PE4*, P_{atm} is the atmospheric pressure and P_{pipe} is the pressure at the pipe.

$$V_{subsample} = V_{trapped} \cdot \left(1 - \frac{P_{atm}}{P_{pipe}}\right) \tag{3.22}$$

Valve *Vent_PE3* located at the top of the collecting tank (which is at atmospheric pressure) is opened in the next step and the substrate moves to this tank due to the pressure difference. After some time, the drain valve *Vent_PE4* is opened releasing pressure until the system pressure is equal to the atmospheric pressure generating the condition for the next sample. This procedure is repeated n times generating a composite sample (*Operation 5*) with a volume $n \cdot V_{subsample}$. Both parameters, number of subsamples n, and volume of trapped air $V_{trapped}$, can be varied to find the configuration that generates the lowest variance σ^2. Variance was calculated as the space correlation between the samples is not known (*Operation 2 and 3*).

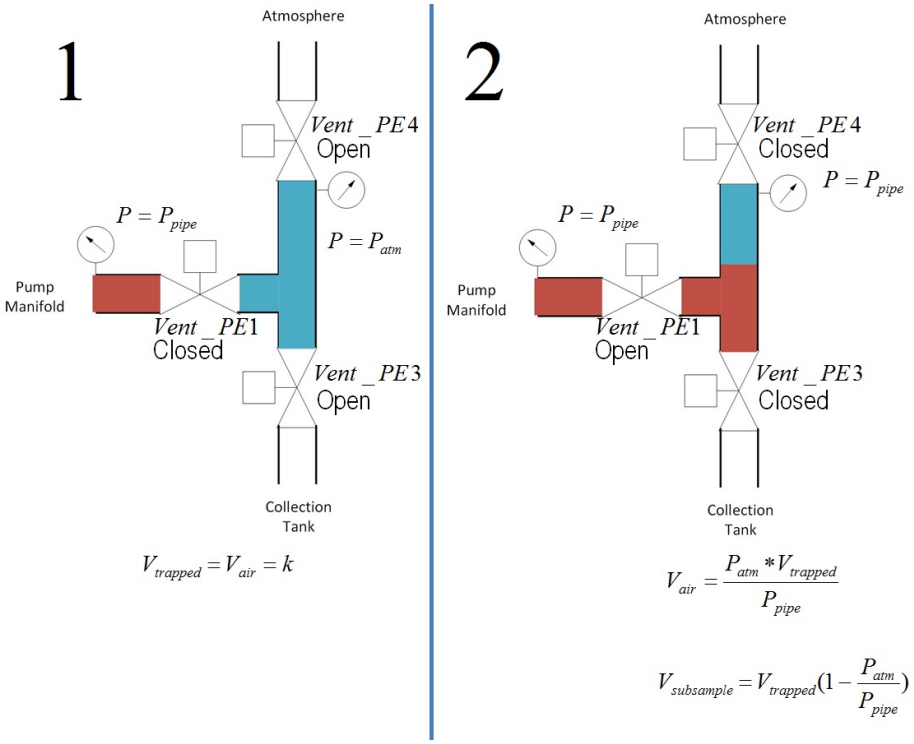


Figure 3.5.: Subsample dosing. 1 Valves position before taking subsample. 2. Valves position after taking the sample. (red = digestate , blue = air)

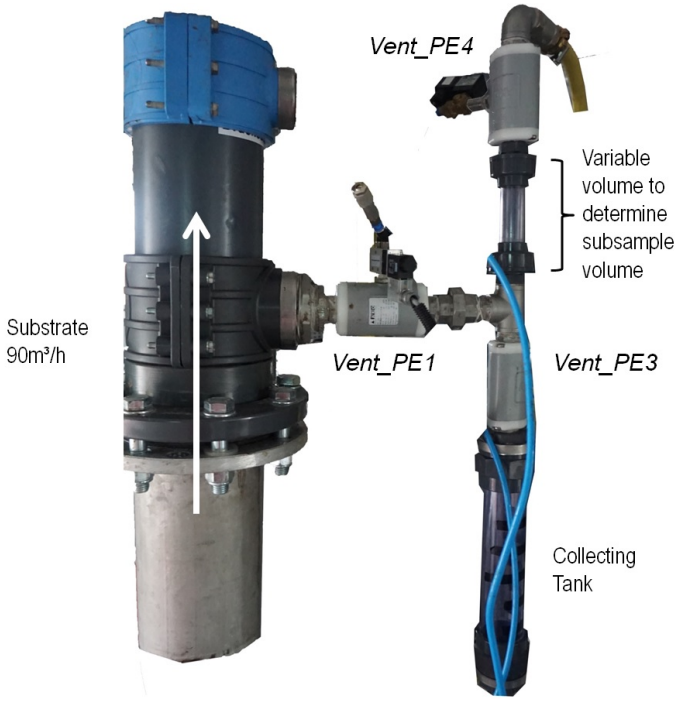


Figure 3.6.: Physical construction of the three valves to define sampling volume according to the trapped air volume, .

• *Step 2 Mixing:* once the samples are collected, they are mixed to decrease heterogeneity (*Operation 4*). The sample is mixed with the help of compressed air, normally available at biogas plants to operate the pneumatic valves or to secure the gas membranes. The valve is located at the bottom of the collecting tank *Vent_DL_TANK* and is protected with a non-return valve.

Compressed air is bubbled through generating a well-mixed substrate. This procedure is repeated several times. Once the sample is well-mixed the valve located at the bottom of the collecting tank *Vent_PE2* is opened allowing the sample to move to the filter.

CO_2 dissolved in the sample generates an overestimation in the VFA as it increases the titrant consumption. In back titration, pH is reduced and then air is added to the sample for $t = 120s$ to reduce CO_2. Using air for mixing may remove CO_2 dissolved in the sample and also strip some VFA, decreasing the VFA content [139].

Nevertheless, this procedure was used for its simplicity and ease of cleaning. The effect could not be quantified but is assumed to be small as pH is not reduced before the mixing and the mixing time is much smaller compared with the back titration ($t < 1s$). Air pressure was set to $1bar$ and the time of exposure of the sample to compressed air minimized using visual inspection of the mixing quality.

• *Step 3 Filtering:* Due to the high solids content in different degradation states it is necessary to centrifuge or filter the sample in order to increase the repeatability of

the analytical measurements [133, 125]. Filtering the sample was chosen as sample pre-treatment (*Operation 6*). The filter unit is divided in two stages: The first has a mesh of 0.5*mm*, the second of 0.1 *mm*.

Material flows to the first stage, but due to the large number of solids, the pressure loss is high and only a small amount of sample passes through the filter. Valve *Vent_PE3* is closed and compressed air is pumped through the valve *Vent_DL_TANK* increasing the pressure and allowing a larger amount of the sample to pass through the first filter. The same procedure is then repeated between the first and second sieve, this time opening the valve *Vent_DL_FILTER*.

The resultant sample has a guaranteed particle size smaller than 0.1 *mm*. Before the sample is pumped to the titration cell the generated over-pressure is released by opening the adjacent valves to avoid affecting pumping volumes.

• *Step 4 Analytical measurement:* The filtered sample is collected and then transferred to the measurement device with a positive displacement pump. In this case an autotitrator was used to determine VFA/TIC ratio but the sample can be sent to any measurement device such as NIRS, Raman or another device. Titration was done with the autotritator TitroLine® 6000 from SI Analytics using the existing routine for VFA/TIC. The routine is based on two-pH points titration to pH 5 and 4.4.

The titration volume suggested in the literature varies from 2 to 150 *ml* [125]. In [139] it was pointed out that titration volume could affect titration results. Accuracy depends on the level of VFA and the titration volume. It is suggested small volumes for high VFA levels and large volumes for low VFA. In [139] was suggested a titration volume of 40 *ml* of four times diluted sample to obtain optimal titration results.

Titration volume was fixed for all the measurements as VFA levels are not known in advance and the levels could change over time depending on the digester situation. Small titration volume was selected due to the characteristics of the sampling and pre-treatment and to minimize the consumption of reactants as many samples can be taken per day.

In a customized titration cell with agitator, the dosing system pumps 5*ml* of filtered sample then dilutes this with 20*ml* of distilled water

Titration starts automatically, and results are saved in a data base. When the titration is finished the dosing system cleans the cell and keeps the electrode submerged in a KCL-solution (3mol/l) to preserve it for the next titration.

• *Step 5 Cleaning:* After the sample is collected and filtered the sampling unit must be cleaned. The cleaning process is divided into several steps to guarantee that the sampling unit is clean and dry for the next sample. Tank tap water is repressurized and used to flush sample remnants into the digester when opening the valve *Vent_PE1*.

Filtration elements have a dedicated cleaning circuit opening valves *Vent_ABFLUSS* for mesh 0.5 mm and *Vent_ABFLUSS_1* for mesh 0.1 mm. After cleaning, com-

pressed air from valve *Vent_DL_TANK* transports the water remaining to the drain. This is important to avoid contamination of the next sample.

The sampling system installed at the research plant is presented in Fig. 3.7 on the next page. All VFA/TIC measurements presented in this work were done with this system.

The sampling device was further developed and it is now commercialized by the company bwe energiesysteme GmbH &Co. KG, see Fig. 3.8 on page 61.

3.4.1. Sampling conditions

Before the device was used to monitor the biogas plant it was necessary to determine the combination of sampling parameters, number of samples n, and volume of trapped air $V_{trapped}$ that generates the lowest variance.

Determination of the sampling parameters was based on the following conditions:

Max volume of composite sampling: This volume is limited by the size of the collection tank located under valve *Vent_PE3* which in the setup has a volume of 1.1 liters. The maximum sample volume was fixed at 600 ml to avoid sample loss when the sample is mixed with compressed air.

Duration of sampling procedure: It is important to guarantee long term implementation of the sampling device, so that no additional work is generated for the operator. For this reason sampling collection must happen during normal pumping operations. This means that no additional pumping is required only to generate a measurement.

According to the feedstock fed, approx 16 m^3 of digestate are generated daily and must be pumped from digester to storage tank. The central pump requires about 10.5 min for this task.

The digestate was pumped 4 times a day to generate 4 measurements per day and attempt to cover the system behavior. For any sampling procedure the maximum available pumping time was fixed at 2.5 min.

Before taking a sample, the central pump operates for $40s$ to ensure that the pump manifold contains only a fresh sample. A subsample is taken every $20s$ while digestate is pumped. This means that from every 0.5 m^3 pumped digestate a subsample is extracted. Depending on the number of subsamples the duration of the sampling procedure is $120s$ for 4 or $140s$ for 5 subsamples.

The total sampling procedure including sample collection, preparation titration and cleaning takes about 25 min. The minimum time between two measurements was fixed at 30min.

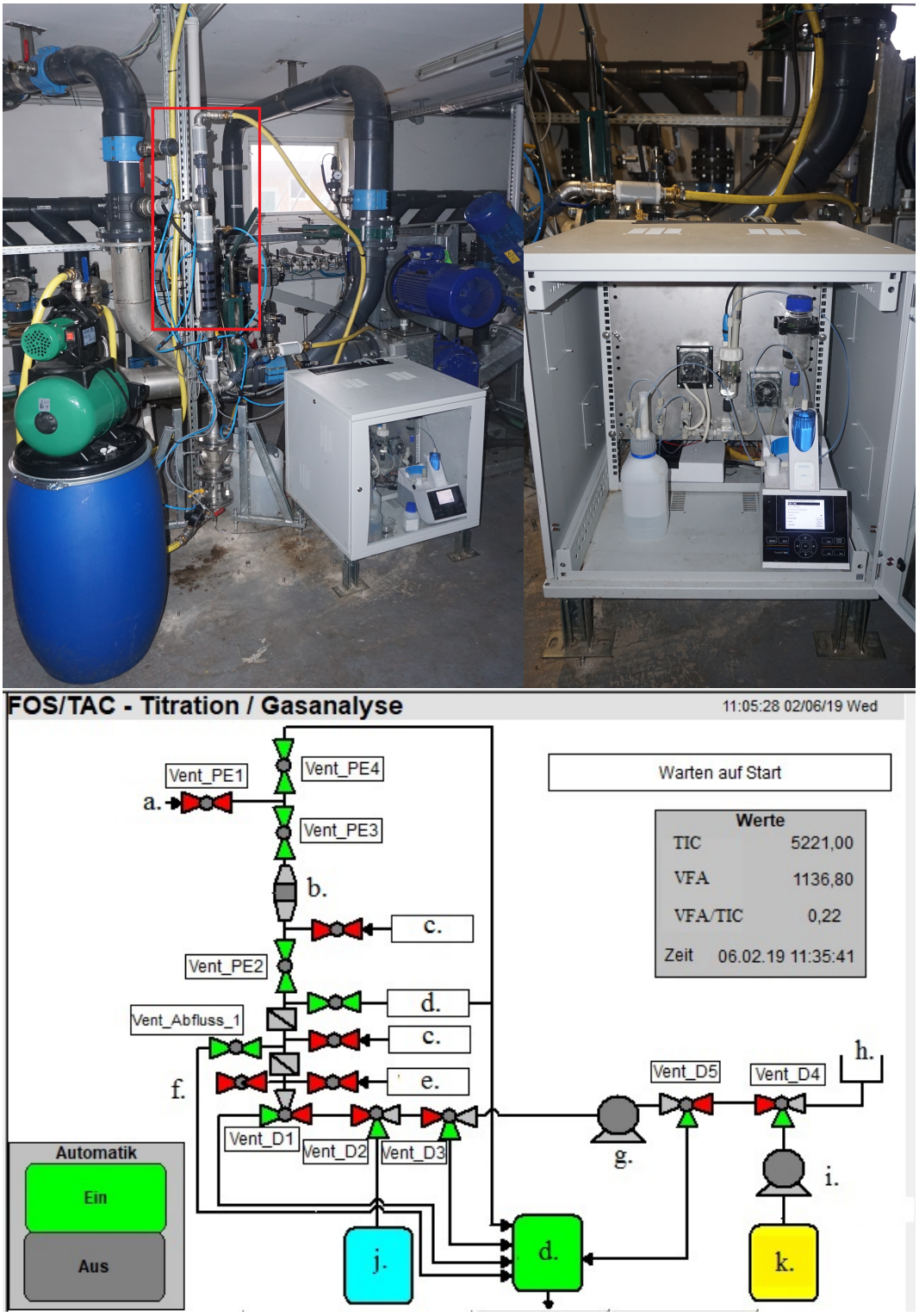


Figure 3.7.: Above left: Sampling system installed at the research plant. Marked sample collection. Above right: dosing unit and titrator. Below: visualization for the operator. (key: a. Connection pump manifold; b. Collecting Tank; c. Pressure air; d. Drain; e. Water; f. Venting; g. Peristaltic dosing pump; h. Titration cell; i. Peristaltic pump; j. Distilled water; k. KCL-solution)

Figure 3.8.: Automated VFA/TIC, commercial application.

3.4.2. Determination of sampling parameters

Before the device was used to monitor the biogas plant it was necessary to determine the combination of sampling parameters, number of samples n, and volume of trapped air $V_{trapped}$ that generates the lowest sampling error.

The main issue here is that the measurements are done in a dynamic system. Concentration of VFA in a digester depends on many factors including interaction of different bacteria groups and archaea, operating conditions, feeding scheme and the addition of new microorganisms (manure feeding).

Dealing with a dynamic system has the consequence that the difference between two measurements could not only be originated by the sampling and measuring system but also result from internal changes in the digester itself.

In order to determine the sampling parameters configuration is necessary to assume that digester state is constant in a short time interval. In that way consecutive measurements should provide the same result and difference can be explained by sampling and analytical errors. Standard deviation σ was selected to describe the spread of the measurements around their mean.

Sampling device can only take a sample at the same time which means that the configuration comparison must be done with measurements from different days. Three different configurations were measured. Operating conditions, agitation and feeding schedule were kept constant. Digester conditions still could vary over time due to substrate characteristics. Maize is collected from a silo at which different varieties are located and is exposed to weather conditions which could also generate changes in the dry matter.

Before a sample was taken the agitation system in the digester was run for 5 min.

Two *V_trapped* configurations with a resultant *V_sample* of 120 ml and 96 ml were tested, see Fig. 3.5. The following configurations were tested:

- 5 subsamples of 120 ml. Total volume 600 ml
- 4 subsamples of 120 ml.Total volume 480 ml
- 5 subsamples of 96 ml.Total volume 480 ml

A summary of the sampling parameters for the configuration with 5 subsamples of 120 ml is presented in Fig. 3.9 on the next page. Composite sampling itself is only 0.024% of the pumped volume, but the initial sample covered approximately 0.126% of digester volume. This value is in the sampling range from (0.1-1%) described as typical for this digester volume by [169].

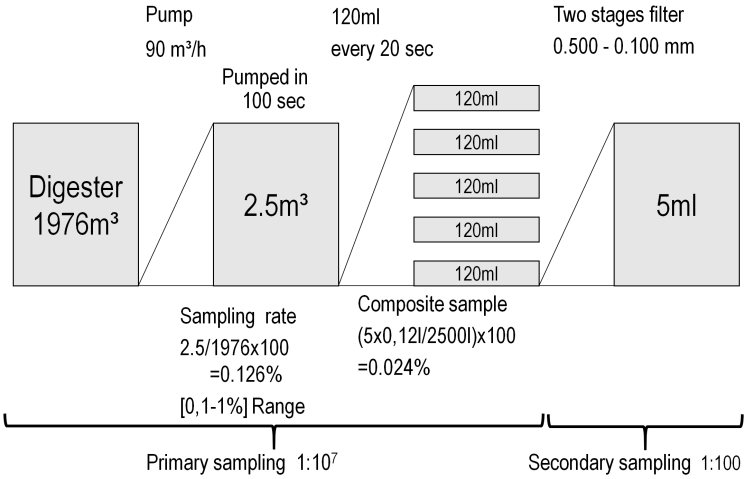


Figure 3.9.: Sampling parameters

3.5. Gas volume measurements

3.5.1. Gas volume assumptions

Gas volume in a double layer system is determined by assuming that the gas storage membrane has the shape of a spherical cap, see Fig. 3.10. Based on this assumption the volume is calculated using the height of the cap h and digester radius r.

First it is necessary to determine sphere radius R at different filling levels measured in this case by the variation of the rope length $\triangle r$ (Rope system) by iteration in the following equations.

$$\theta \cdot R = 2 \cdot r + \triangle r$$

$$\sin(\theta) = r/R$$

With the sphere radius R the height of the cap h can be calculated. After that using the volume equation for a spherical cap the gas volume is calculated.

$$V = \frac{\pi \cdot h \cdot (3r^2 + h^2)}{6} \tag{3.23}$$

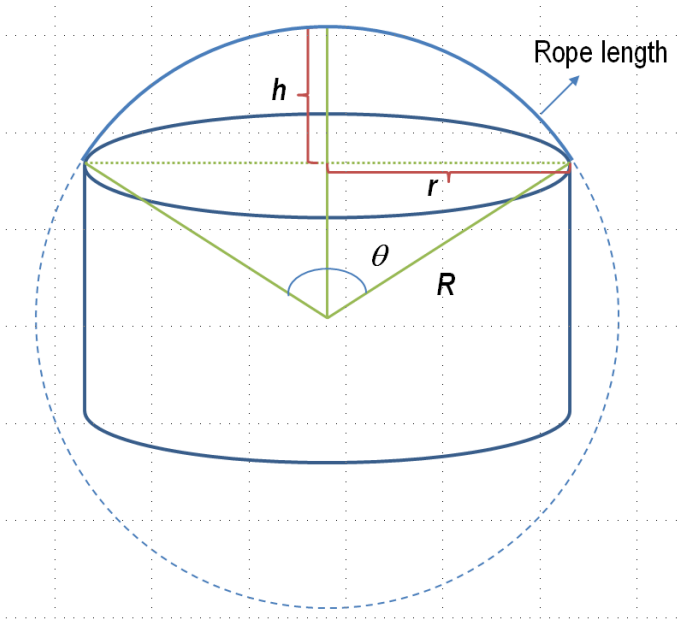


Figure 3.10.: Gas storage membrane with spherical cap shape.

The relationship of gas storage volumes to $\triangle r$ in a $22m$ diameter digester is presented in Fig. 3.11. Note that at lower gas volumes a small variation of $\triangle r$ generates a large volume change which makes the measurements at low gas volumes inaccurate.

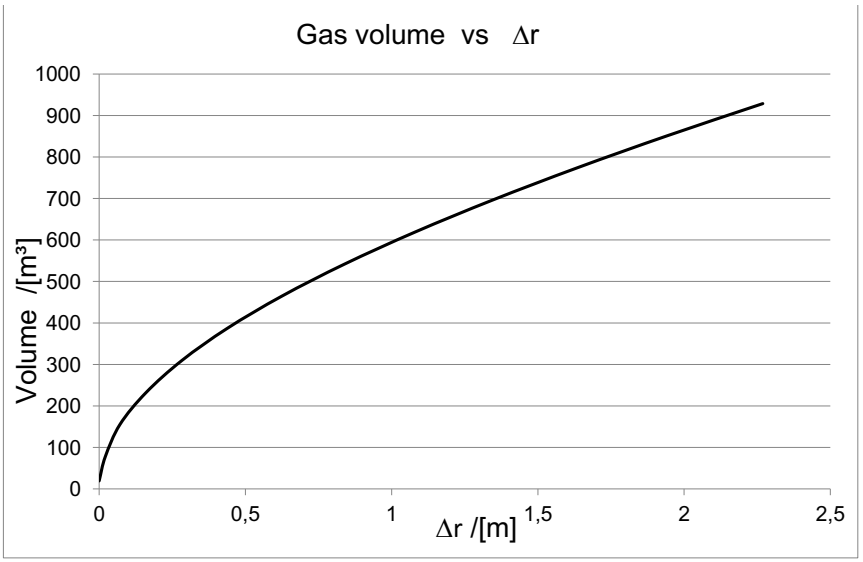


Figure 3.11.: Gas volumes vs $\triangle r$ for a 22 meter diameter digester

Unfortunately, the assumption that the gas membrane is a spherical cap is not fully correct because membrane shape can be irregular. The main reasons are:

- Pressure in the gas storage space (below gas storage membrane) and between the membranes is almost identical [151]. Because of low pressure difference between the containment and the stored gas digester, this means that the assumption of spherical cap is only an approximation.
- The area of the membrane is fixed and has been manufactured with the shape it will have at full capacity, see Fig. 3.12. Many of the plants in Germany have a conical shape in the gas storage and weather protection membrane.
- The internal air flow from the supporting fan and the location of the gas extraction point may also modify the membrane shape [150].
- The force generated by the rope with the attached weight also affects the membrane shape.

Figure 3.12.: Photo between membranes without straps

The company Baur Folien GmbH has developed a “calming system” where elastic straps are installed over the gas storage membrane, see Fig. 3.13 on the following page. The straps confined the gas to the center generating a shape like to a spherical shape allowing use of the equation in 3.23.

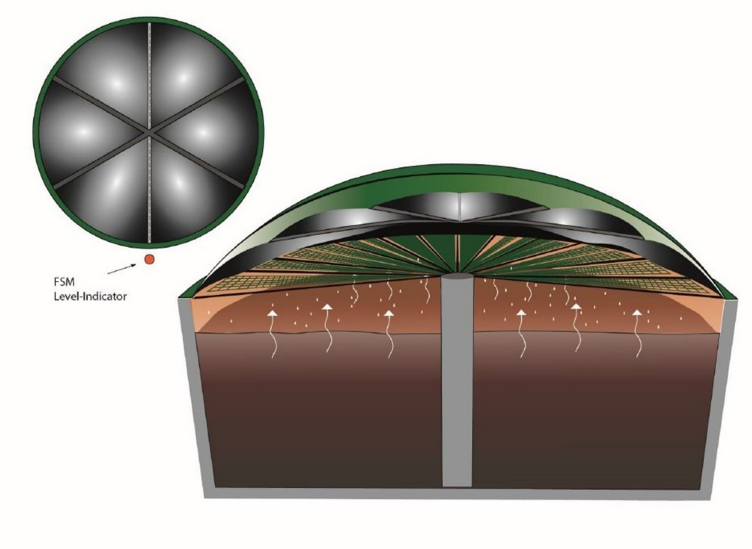


Figure 3.13.: Calming system. Source: Baur Folien GmbH

The Baur "calming system" was installed in the agricultural biogas plant used in this research, to improve gas production measurements. Even though measurement accuracy was increased there is still error due to membrane shape which will bias the results, see Fig. 3.14 on the current page. The original membrane shape is conical and due to the elastic straps, the shape tends to be spherical which generates folds that may imply that different stored volumes will have the same measurement.

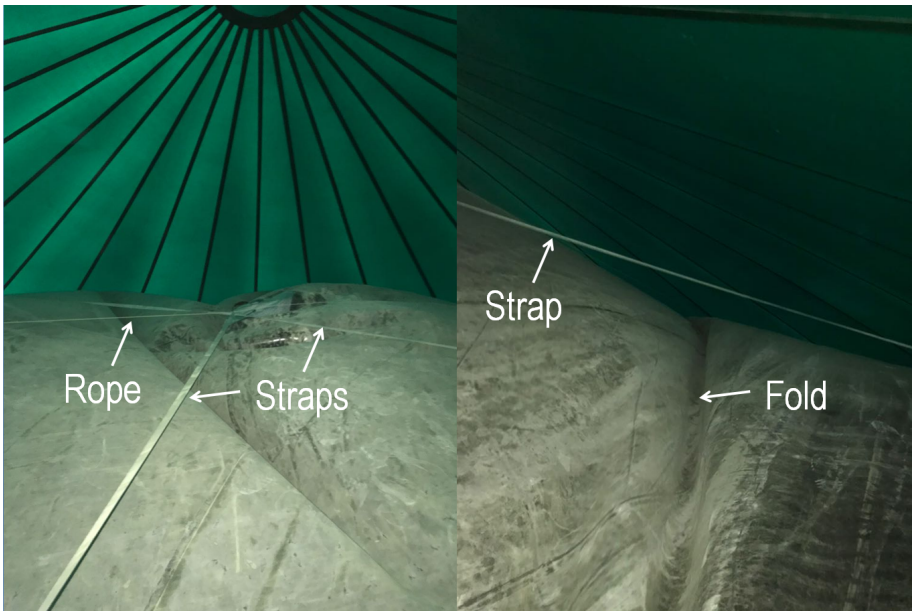


Figure 3.14.: Photo of "calming" elastic straps in the. Left: crossing point of straps and rope. Right: fold generated by straps.

3.5.2. Operational range gas storage.

As already presented in Fig. 3.11, for lower gas volumes the measurements will not be accurate. In addition, at lower levels the membrane will be substantially folded which also increases the risk of measurement error. In [151] a minimum desired operating limit was defined by 5% of total gas volume with water gauge measurements. In [155] a measurement delay was found in the range of 0 to 36% of the gas storage. It was explained with an empty storage that starts to be filled. In this case the membrane starts to rise but only when the volume is large enough the area under the rope starts to rise up due to the pressure generated from the counterweight required to extend the rope. It is however difficult to define at which level the measurements become reliable due to the membrane folds or delay in the measurements, so that the minimum desired operating limit was defined at 20% of the gas storage for this work.

As can be seen in Fig. 3.11 there is almost a linear relation between gas volume and rope length $\triangle r$ at large volumes that enables reliable measurements. The main issue is when the gas storage volume reaches its maximum. This can be detected when the gas storage membrane touches the external membrane causing a rise in store gas pressure. In order to determine the maximum allowed operating limit a series of measurements were done on the commercial plant of this study.

3.5.3. Gas management

The purpose of the gas management is to keep the filling levels of the tanks in a range where the measurements are as accurate as possible. In the case that one tank is out of the operating range, gas should be moved between the connected tanks until the tank returns to the desired range. A gas management control system was developed and implemented in the commercial plant of this thesis.

Weight at the pressure regulated valve was fixed at the same level in the digester and storage tank, see Fig. 2.4. Gas pressure in a tank is modified by changing the frequency (or revolution per minute, rpm) of the supporting fan, in that way a pressure gradient is generated which allows moving gas in the desired direction.

Gas management control philosophy:

- The difference between digester volume VN_D and digestates storage volume VN_S in percentage was fixed to 5%. $|VN_D - VN_S| \leq 5\%$. The logic behind this restriction is that both tanks will be at the same level and only if there is not gas or if the gas storages are full will the levels be outside operating ranges.
- $If\ VN_D + 5$ then, rpm fan in the storage rpm_S is reduced to a minimum rpm_{S-MIN}. In that way gas pressure in digester P_{gD} will be higher than gas pressure in the digestates storage P_{gS}, $P_{gD} > P_{gS}$.

- $If\ VN_S - 5$ then, rpm fan in the digester rpm_D is reduced by a factor rpm_{D-MIN}. In that way gas pressure in digestates storage P_{gS} will be higher than gas pressure in digester P_{gD}, $P_{gS} < P_{gD}$
- $If\ P_{gD} < 0.5mbar\ or\ P_{gS} < 0.5mbar$ then, rpm is returned in both tanks to its nominal value ($2815/min$). This restriction is important because the fan gives structural support to the membranes. Minimum snow load considered is $5kg/m^2$. This assumption is because the tanks are heated, and the membrane is always warmer than the outside temperature.
- $If\ |VN_D - VN_S| \leq 5\%$ then, rpm is returned in both tanks to its nominal value.

The control system was programmed and implemented in the test plant including safety measurements, to return supporting fans to nominal frequency in the event of a malfunction or after power cut [170, 171, 172]. See Fig. 3.15.

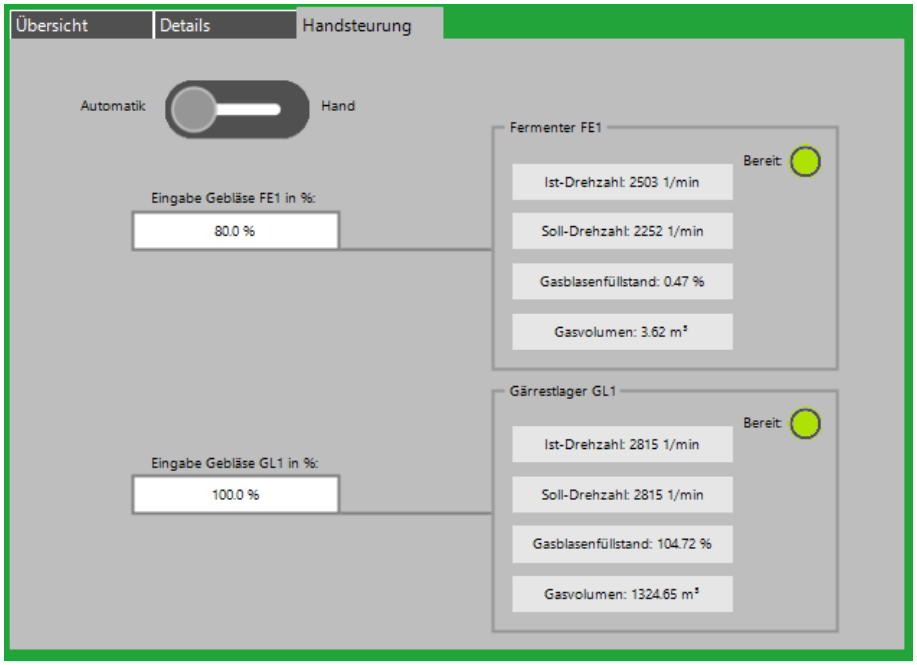


Figure 3.15.: Control interphase gas management. (English key: Fermenter Digester Gärrestlager Digestates storage tank; Ist-Drehzahl Actual rotational speed; soll-Drehzahl Target rotational speed; Gasblasenfüllstand Gas storage level; Gasvolumen Gas volume)

The main issue was to determine which are the rpm_{S-MIN} and rpm_{D-MIN} which are not necessarily the same, even if both tanks have the same fans. Gas pressure is determined by many factors, one of them is air pressure between the membranes. P_{aD} for the digester and $P_{aS}$for the storage. P_{aD} and P_{aS} depend on the fan pressure loss which is related to the transverse section which the air passes through. This area depends on the tank dimensions and fill level of the gas storage.

Different gas storage level and digester dimension will modify the fan operating point and therefore is it possible to have different operating pressures at the same rpm. For example in Fig. 3.16 Tank 1 has an operating curve with higher pressure losses than Tank 2. In case it is necessary to move gas to Tank 1 a larger frequency reduction is required in order to have a lower pressure than Tank 2.

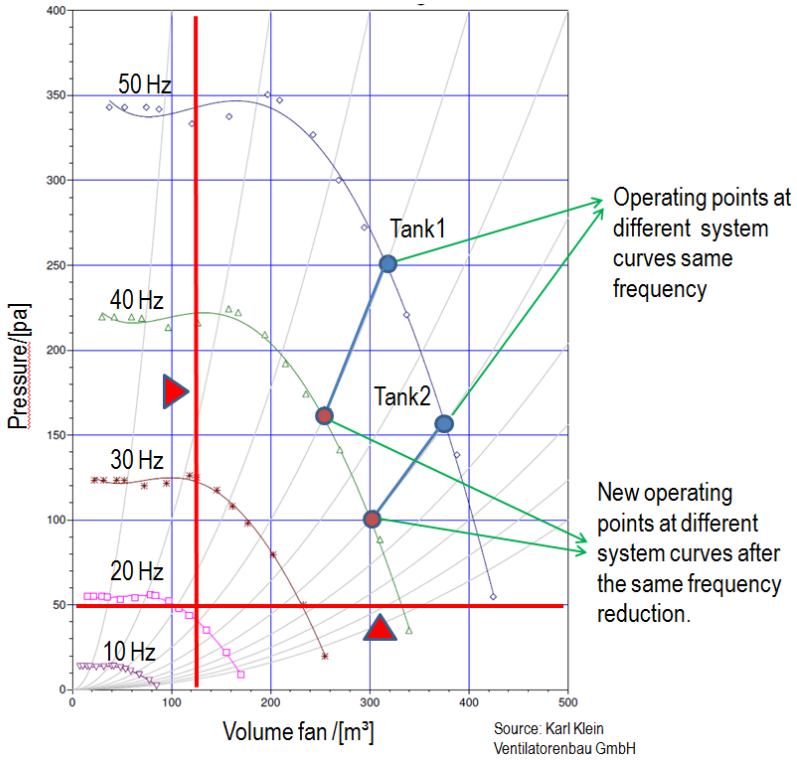


Figure 3.16.: Operating range fan. (red lines). Operating curve of the installed fan at digester and digestates storage tank. Nominal fan speed is $2815/min$ at $50Hz$.

This implies that finding the fan rpm at a fixed gas storage level that produces certain pumped volume and generates the required gradient is not enough. This is because once the gas fill level changes the pressure loss will be different and a different pumped volume and pressure gradient could be generated

An additional restriction is required to guarantee the stability of the system and that is the minimum pumped air volume between the membranes should be equal to the gas volume consumed by the engine. This is of special relevance when the plant should deliver power on demand due to load variations. In the test plant there is only one engine $250kW$ consuming $133m^3/h$ on average, but in the case of an expansion i.e to $500kW$ gas consumed will double. In this case the existing fan must deliver double the volume to fill the generate void. If the fan does not have the capacity the external membrane will not be completely extended making it vulnerable to wind distortions so that in high winds the system can be unstable.

This restriction is valid if we have only one tank. In a multiple storage system like the plant used in the study, gas flow from each tank to the engine will depend on the pressure loss of each line.

The approach to determine rpm_{S-MIN} , rpm_{D-MIN} is to start with a small reduction of the fan rpm that generates a pressure gradient and a minimum gas volume. This measurement must be verified at different filling levels to guarantee the stability of the system.

In order to verify rpm_{S-MIN} , rpm_{D-MIN} selection and determine the operating conditions the following equipment was installed in the plant, see Fig. 3.18 on the following page.

- Air volume pumped between membranes was measured with an anemometer Kimo VT 200 adapted into the pressure regulation valve, like [173] A vane probe with a 70 mm diameter was installed in a T-junction, see Fig. 3.17 on the current page. Selected anemometer has an integrated temperature measurement to adjust the volume.
- Temperature in the gas room was measured with a Omnigrad T TST434. Resistance thermometer installed at the over under pressure relief valve.
- Fan pressure was measured with a Cerabar M PMC51 installed at the inlet pipe connected to the gas storage.

Figure 3.17.: Air flow measurement in pressure regulating valve

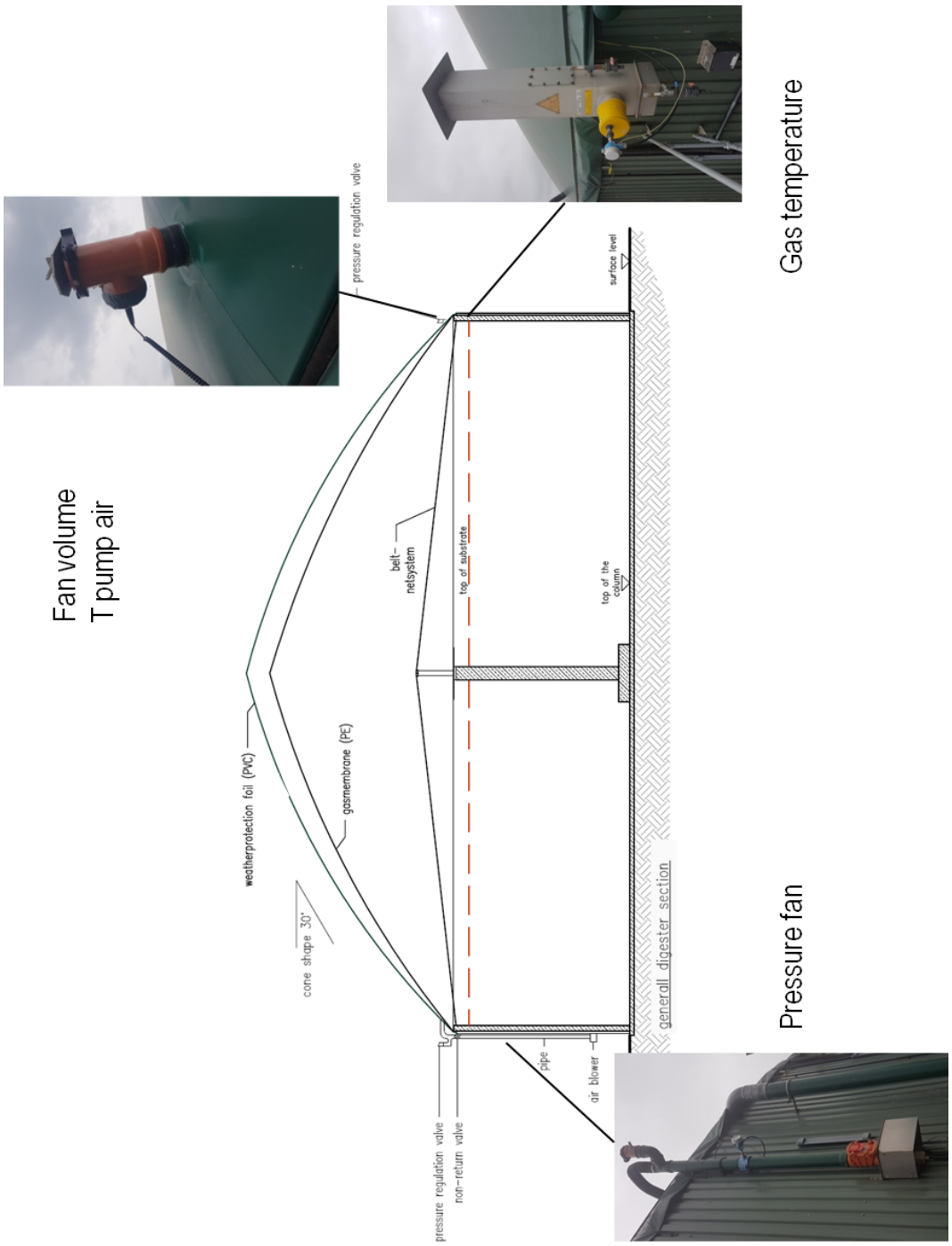


Figure 3.18.: Measurement equipment gas storage. Includes parameters name

3.5.4. Temperature and pressure correction gas volume.

It is necessary to estimate the gas temperature $T_{g\,k,i}$ and gas pressure $P_{g\,k,i}$ in each k gas storage at time i in order to correct its gas volume.

In the case of gas temperature as it was observed in Fig. 4.11 when the gas storage membrane is not touching the gas membrane, the gas temperature can be estimated based on the ambient temperature. Also important here is that gas temperature varies with the digester dimensions and for that reason it has to be measured at the different digester sizes which make part of the biogas plant.

Regarding the pressure due to its low variation (about1$mbar$) it was not considered for the calculation. Two volume corrections have to be consider the first one due to the temperature expansion and the second due to its water vapor content.

Volume at operating conditions is calculated with the following equation. Where $VN_{k,i}$ is the estimated volume (normalized) at time i of gas storage k from the biogas , $V_{k,i}$ its correspondent volume at the operating temperature and $TN = 273.15°K$.

$$\frac{VN_{k,i} \cdot T_{g\,k,i}}{TN} = V_{k,i} \tag{3.24}$$

Water vapor content in the gas which is dependent on its temperature also increases its volume. The table Tab. 3.1 presents the correction factor for different temperatures.

	Temperature								
	5	10	15	20	25	30	35	40	45
Water content/[g/m^3]	6.8	9.4	12.8	17.3	23.1	30.4	39.7	51.2	65.3
Water vapor content/[l/m^3]	8.5	11.7	16.0	21.5	28.7	37.9	49.4	63.7	81.3
Correction factor $WP(T_{g\,k,i})$	0.991	0.988	0.984	0.978	0.971	0.962	0.951	0.936	0.919

Table 3.1.: Water vapor correction factor . Source[148]

Including water vapor correction equation 3.24 is modified to 3.25. $VM_{k,i}$ is the measured volume of the k gas storage of the biogas plant in the interval i.

$$\frac{VN_{k,i} \cdot T_{g\,k,i}}{TN \cdot WP(T_{g\,k,i})} = VM_{k,i} \tag{3.25}$$

As the gas temperature in the different storages may vary, it is necessary to apply equation 3.25 to each of the gas storages in the biogas plant.

In the case of a two tanks biogas plant with one digester and one storage the total measured gas volume TVM_i is

$$\frac{VN_{D,i} \cdot T_{g\ D,i}}{TN \cdot WP(T_{g\ D,i})} + \frac{VN_{S,i} \cdot T_{g\ S,i}}{TN \cdot WP(T_{g\ D,i})} = TVM_i \tag{3.26}$$

The difficulty to apply equation 3.26 for the prediction model is that a total gas storage GS_i equation 3.19 can be generated by adding different combinations of $VN_{D,i} + VN_{S,i}$. This means that different corrections can be applied depending on the gas storage volumes.

In this thesis an active gas management was developed and implemented, see sec. 3.5.3. This system allows the operator to actively move the gas between the storages keeping them at the same percentage level $|VN_D - VN_S| \leq 5\%$.

In this case the relation between storages volume is constant K and the following equations are valid and replacing in equation 3.19

$$\frac{VN_{D,i}}{VN_{S,i}} = K$$

$$VN_{D,i} + VN_{S,i} = GS_i$$

$$VN_{S,i} \cdot (1 + K) = GS_i$$

$$VN_{S,i} = \frac{GS_i}{(1+K)} \qquad VN_{D,i} = \frac{K \cdot GS_i}{(1+K)} \tag{3.27}$$

After replacing in equation 3.26 the terms obtained in equation 3.27 is possible to find the correction factor $CF(T)_i$. In case of the test plant $K = 774m^3/1264m^3 = 0.6123$.

$$GS_i(\frac{K \cdot T_{g\ D,i}}{(1+K) \cdot TN \cdot WP(T_{g\ D,i})} + \frac{T_{g\ S,i}}{(1+K)TN \cdot WP(T_{g\ S,i})}) = TVM_i$$

$$CF(T)_i = \frac{K \cdot T_{g\ D,i}}{(1+K) \cdot TN \cdot WP(T_{g\ D,i})} + \frac{T_{g\ S,i}}{(1+K)TN \cdot WP(T_{g\ S,i})} \tag{3.28}$$

3.6. Gas production calculation

Gas volume levels from digester $VM_{D,i}$ and storage tank $VM_{S,i}$ are obtained with the spherical cap approximation, see Fig. 3.11 and its corresponding rope length $\triangle r_D$ and$\triangle r_S$. Gas volumes are normalized to 0°C and 1bar pressure and after that water vapor correction (see Tab. 3.1) is applied obtaining $VN_{D,i}$and $VN_{S,i}$. Temperature and pressure of each storage are continuously measured. Normalized values are saved in memory every 30sec.

Gas flow meter provide hourly values normalized to 0°C and 1 bar pressure. These values are also saved every 30 sec $GCHP_i$

Gas production in a min is calculated as the difference between two measurements and the CHP gas consumption

$$G(30s)_i = VN_{D,i} + VN_{S,i} - VN_{D,i-1} - VN_{S,i-1} + GCHP_i/120 \tag{3.29}$$

Hourly gas production can be calculated by multiplying gas production in 30 s by 120, but this results in a time series with large variations that may be generated by strong wind conditions or temperature effects and for that reason it was not selected, see Fig. 3.19.

$$G(hour)_i = G(30s)_i \bullet 120 \tag{3.30}$$

Three different statistics were used to minimize the large variations previously mentioned in hourly gas production estimation.

3.6.1. Simple Moving Average (SMA).

The number of observations is Nob is used to smooth the data assigning weights $1/Nob$ to the last recent Nob observations and weight zero to all other observations [174]. Large Nob values smooth out short terms fluctuations but also implies that information about short term trends is lost.

$$G(30s)_{i,SMA} = \frac{1}{Nob} \sum_{i-Nob}^{i} G(30s)_i \tag{3.31}$$

3.6.2. Central Moving Average (CMA).

It is like the SMA but considers the same number Nob of data at both sides of the time series. Assigned weights will be in this case equal to $1/(2Nob + 1)$. The

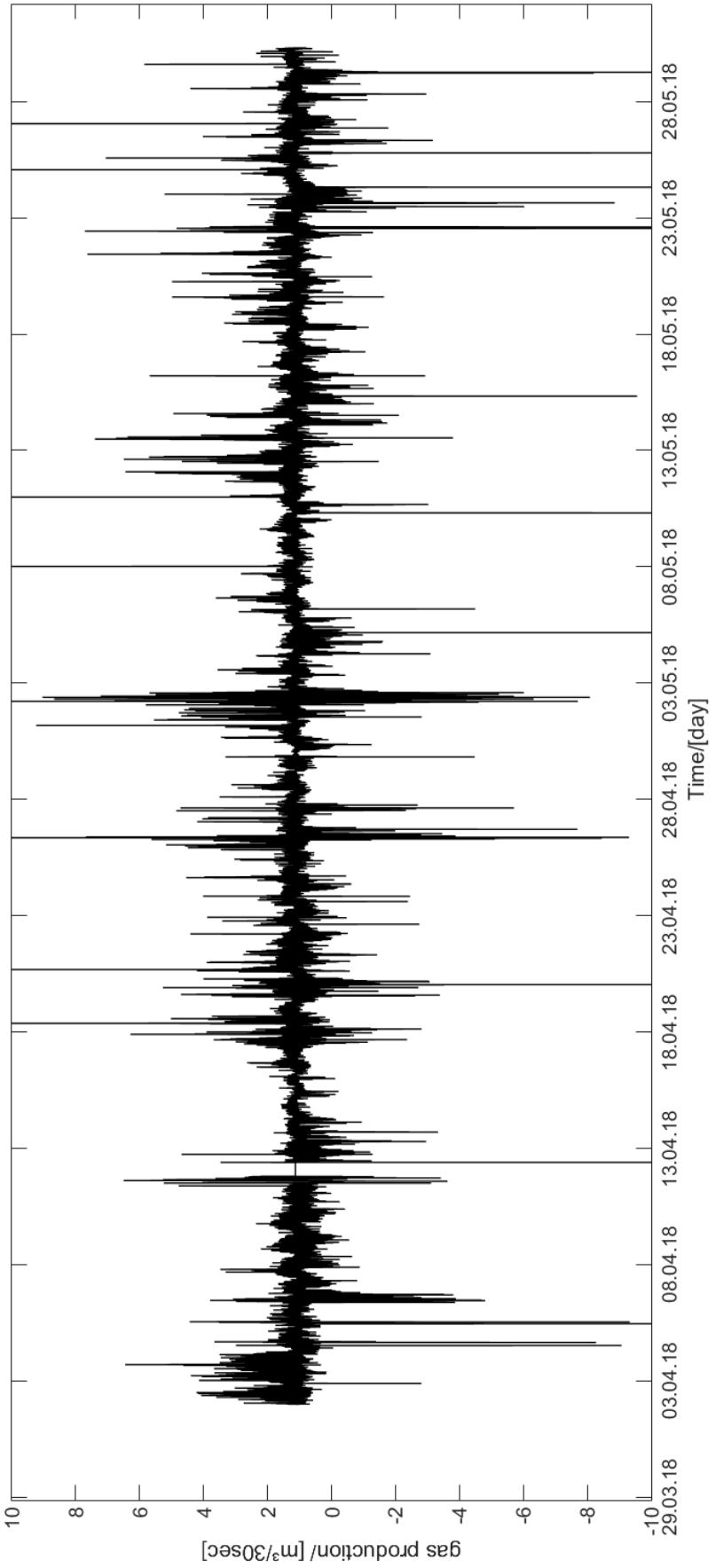


Figure 3.19.: Gas production every 30 sec

idea was to determine if information about the current biogas production can also be recovered including Nob values in the future. The main issue is that it is not possible to provide the operator with current production values as there is always a delay of $Nob \cdot 30s$.

$$G(30s)_{iCMA} = \frac{1}{2Nob - 1} \sum_{i-Nob}^{i+Nob} G(30s)_i \tag{3.32}$$

3.6.3. Moving Median (MM).

The median is the middle observation in rank order (or order of value). Outliers can still affect SMA and CMA calculation for that reason median is an alternative to avoid these measurements. MM has the same delay as CMA

$$G(30s)_{iMM} = med(G(30s)_{(i-Nob)}, .., G(30s)_i, .., G(30s)_{(i+Nob)}) \tag{3.33}$$

3.6.4. Statistics comparison to determine gas production

A comparison is presented for two month measurements of $G(30s)_i$ to select the statistics that better fits hourly gas production. Due to biogas production high dynamics observed in Fig. 4.3 on page 83, the longest proposed span period for statistics is 60 min in order to avoid information lost. Accumulated gas production in the last 60 min was also used for the model estimation, see sec. 3.2.3. A shorter 10 min data span was also calculated to identify short term trends. The selected statistics should only generate positive gas. Hourly gas production was calculated using equation 3.30.

Negative gas production was obtained in all the statistics using a 10 min span for the hourly gas production calculation and for that reason was not selected. SMA (see Fig. 3.20) and CMA (see Fig. 3.21) present similar values while the use of MM (see Fig. 3.22) generates smother gas production curves which could imply that some information is lost.

SMA was the selected statistical model that corresponded to the model definition and current biogas production is available to the operator without delay.

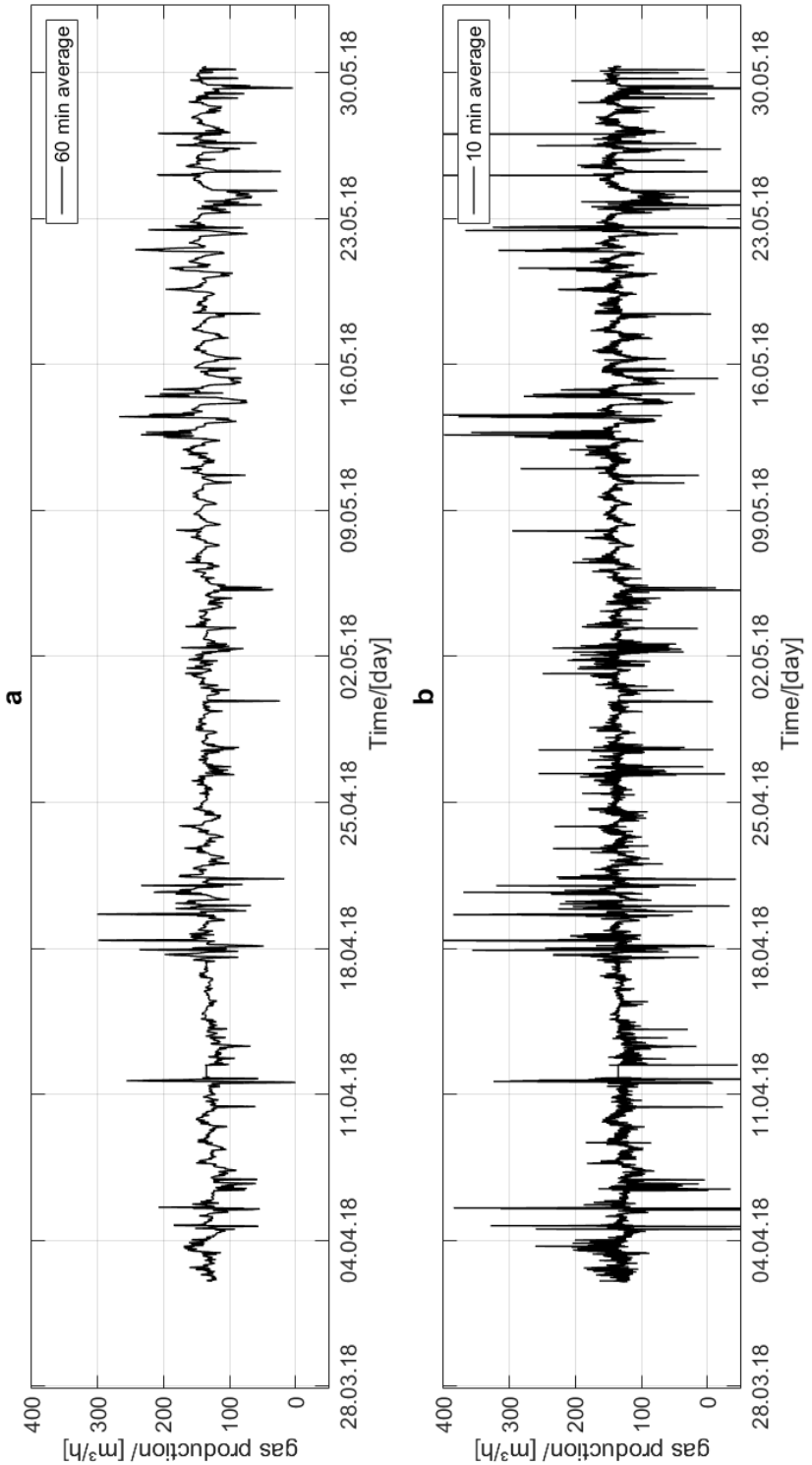


Figure 3.20.: Hourly gas production. a) Simple moving average 60 min span.b) Simple moving average 10 min span

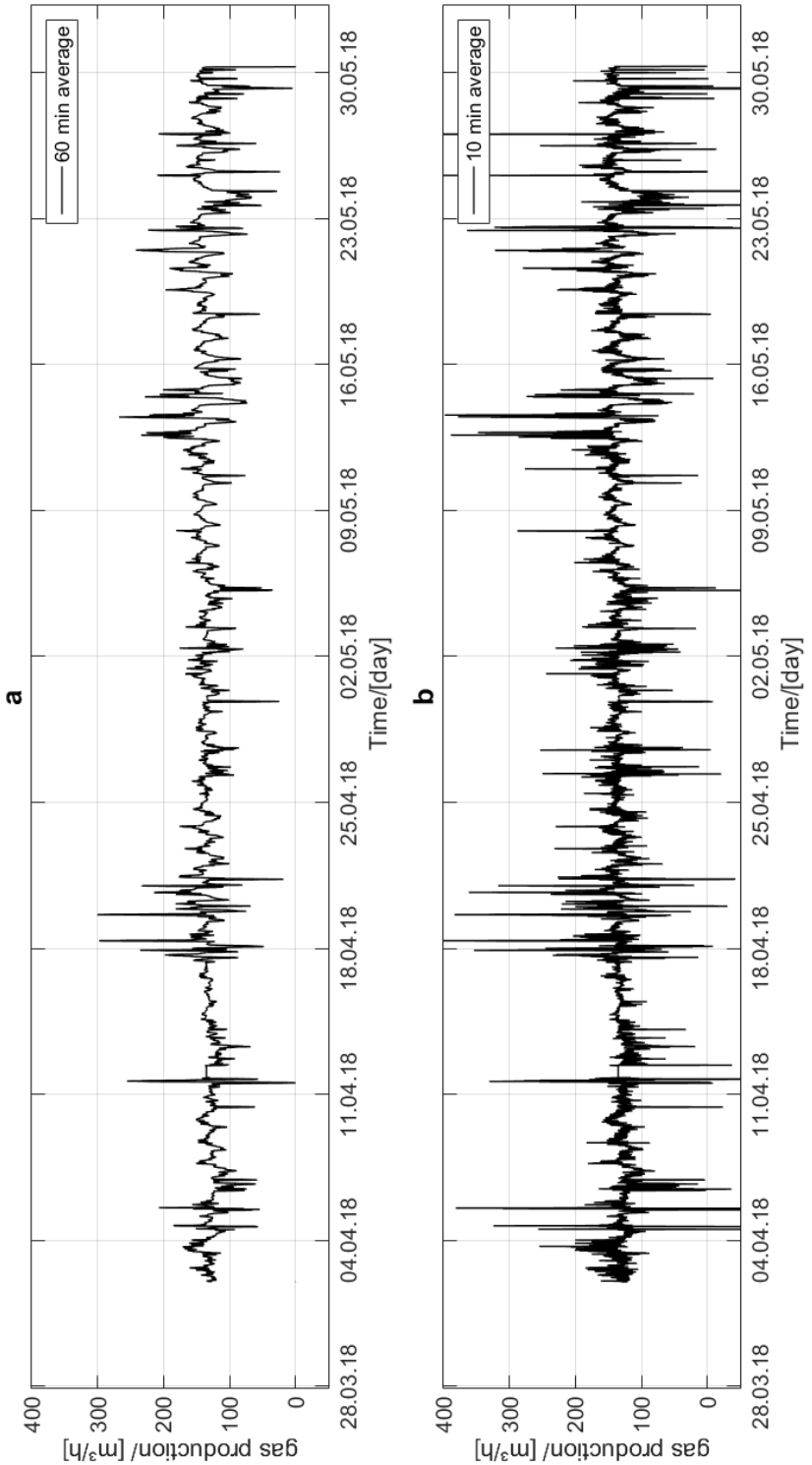


Figure 3.21.: Hourly gas production. a) Central moving average 60 min span.b) Central moving average 10 min span

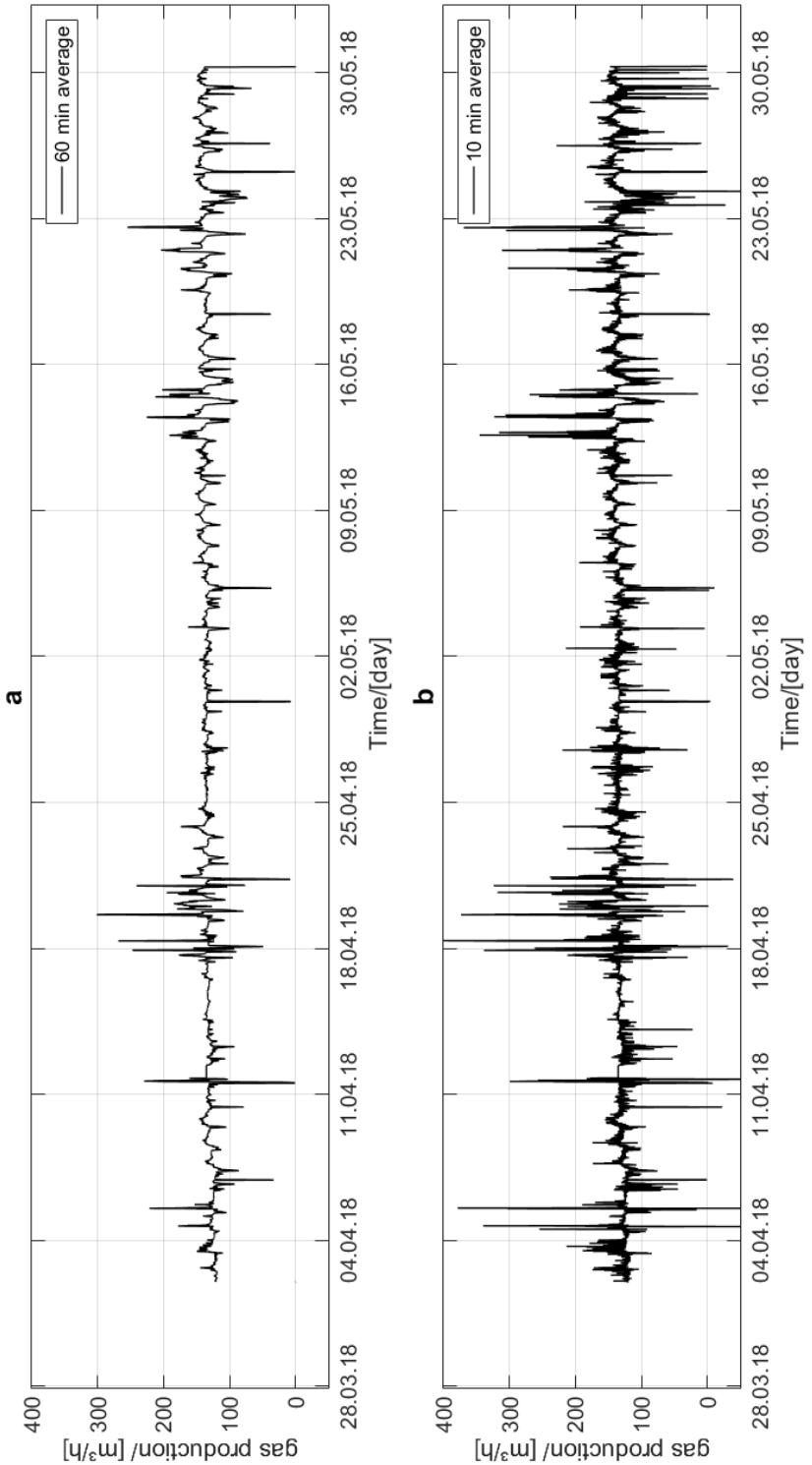


Figure 3.22.: Hourly gas production. a) Moving median 60 min span.b) Moving median 10 min span

4. Results

4.1. Biogas yield curves in the lab reactor

To determine the step response of maize silage for a single feeding, 3 different sets of measurements were developed, see Tab. 4.1.

As a pre-condition to start a set of measurements, the biogas production of the digester was at minimum level, and its value remained constant. This condition was required to minimize the effect of previous feedings. An interval of at least 2 days was required between the last feeding and the start of a new set of measurements. The characteristics of the substrates are presented in Tab. A.1 on page 138 position #1 (Analysis for lab reactor 1).

OLR	$3kg\,oDM/(m^3 \cdot day)$	$4kg\,oDM/(m^3 \cdot day)$	$3{,}6kg\,oDM/(m^3 \cdot day)$
HRT	113.16 d	84.86 d	94.3 d
feeding quantity	95.44 g	127.26 g	114.53 g (split in 2)
feeding interval	Single feeding	Single feeding	every 12 hours
starving time	130 h	60h	130 h

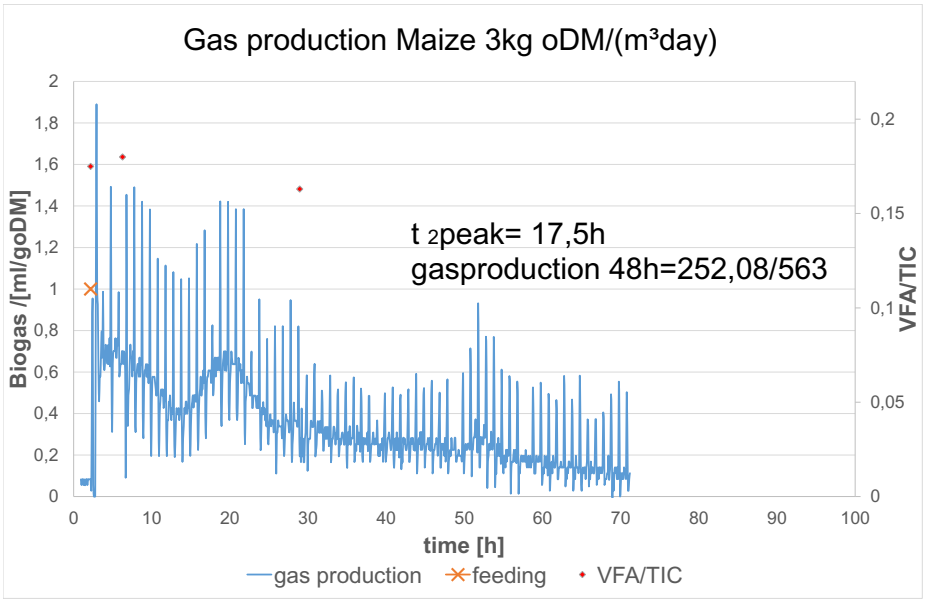
Table 4.1.: Feeding schedule for lab reactor 1 maize silage

Fig. 4.1 and Fig. 4.2 present the first two sets of measurements at different OLR. Biogas degradation curves present two production peaks. The time of the second peak was different in both measurements, as was accumulated gas production in the first 48 hours. Methane concentration reduced after the feeding but increased over time.

The result of the continuous feeding schedule is presented in Fig. 4.3. There is an increase of biogas production immediately after the feeding. A second peak generated by the single feedings, is not present, see Fig. 4.1. Methane concentration is feeding dependent.

In the three sets of measurements VFA/TIC ratios were reasonably constant and at a low level characteristic of a stable system.

Due to the absence of the second peak in the continuous feeding schedule, the step response for maize silage was obtained from lab measurements using the exponential



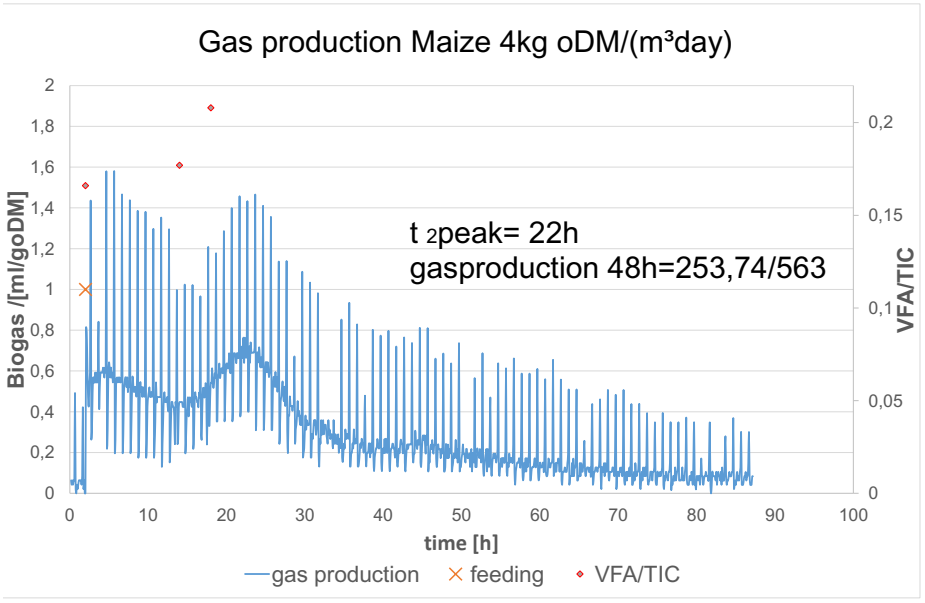
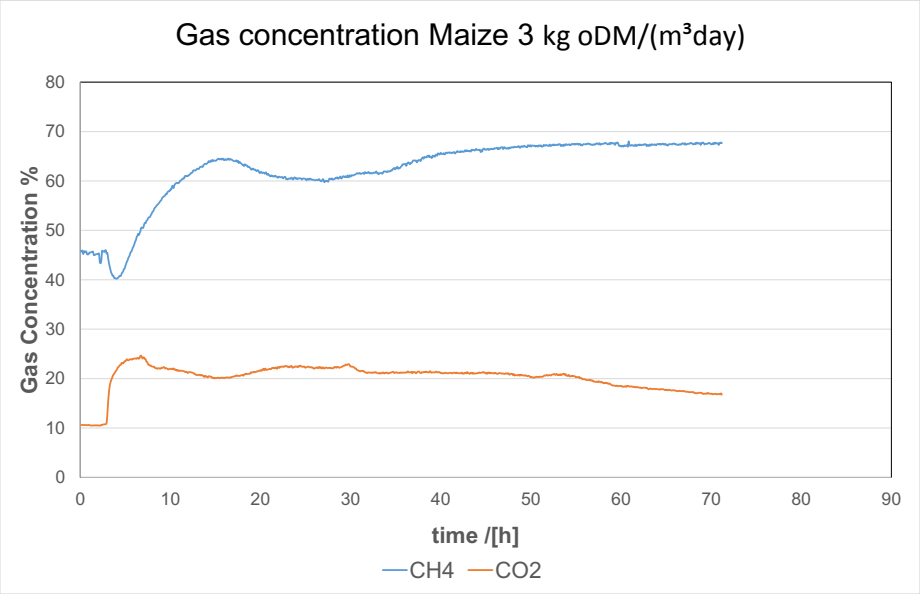


Figure 4.1.: Gas production measurements lab reactor 1a)Single feeding $3kg\,oDM/(m^3 \cdot day)$ b)Single feeding $4kg\,oDM/(m^3 \cdot day)$



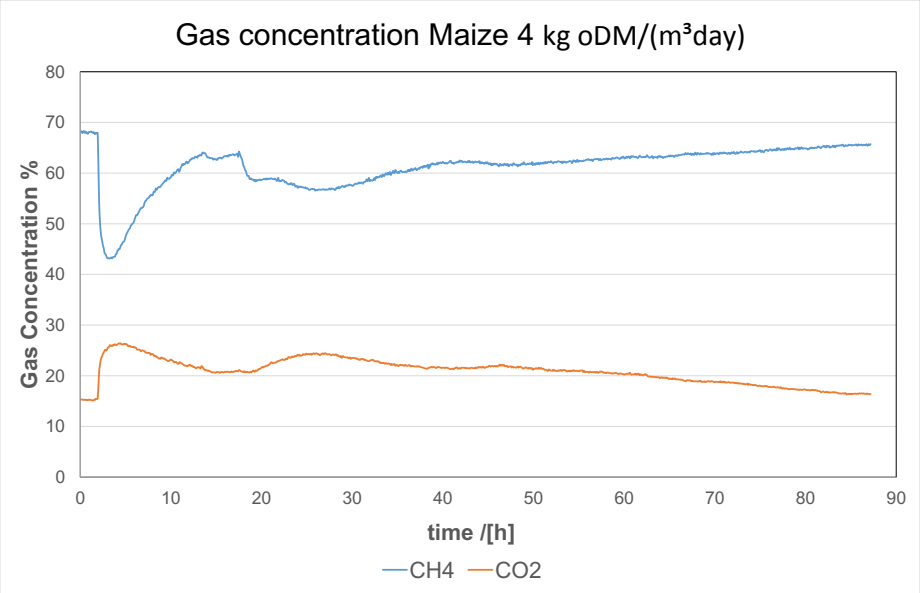
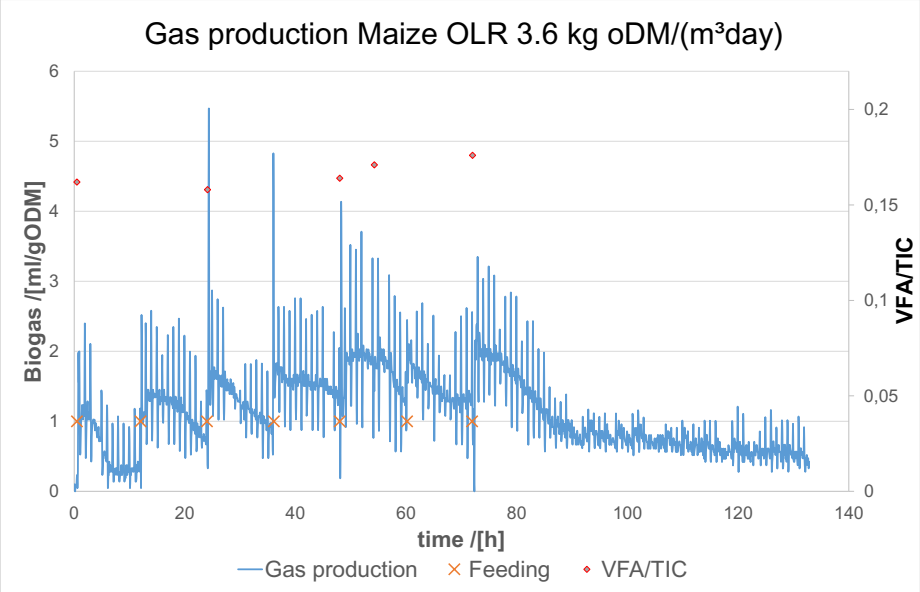


Figure 4.2.: Gas concentration measurements a)Single feeding $3kg\,oDM/(m^3 \cdot day)$ b)Single feeding $4kg\,oDM/(m^3 \cdot day)$



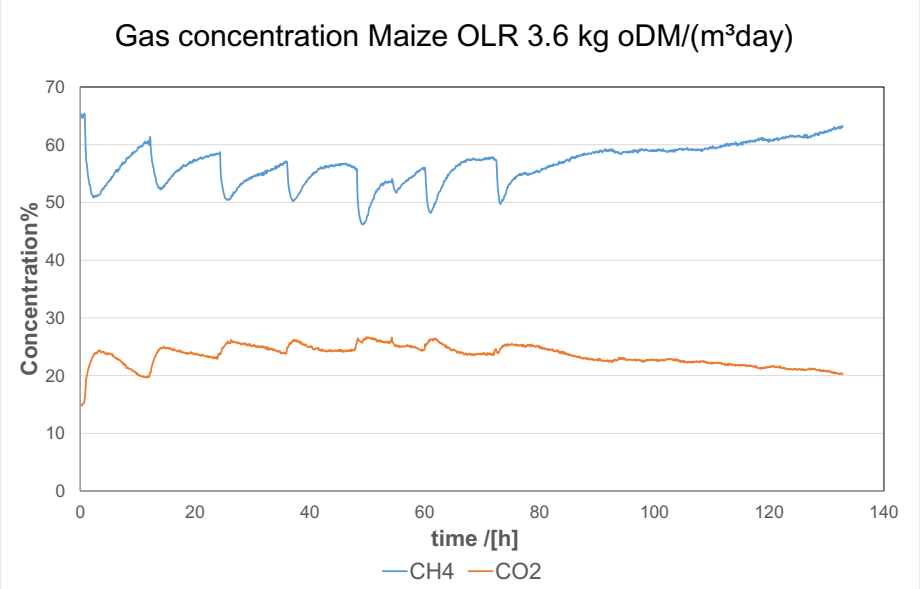


Figure 4.3.: Continuous feeding measurements lab reactor 1 a) Gas production $3.6kg\,oDM/(m^3 \cdot day)$ b) Gas concentration $3.6kg\,oDM/(m^3 \cdot day)$

equation 3.1 on page 42. Fitting is presented in Fig. 4.4, and the single feeding step response is in purple and its equation is the following.

$$f(t) = \begin{cases} \frac{1{,}7 \cdot t}{\frac{1}{6}} & 0 < t < t_{peak} \\ 1{,}7 \cdot e^{-0{,}38 \cdot t} & t_{peak} < t < t_{max} \end{cases} \tag{4.1}$$

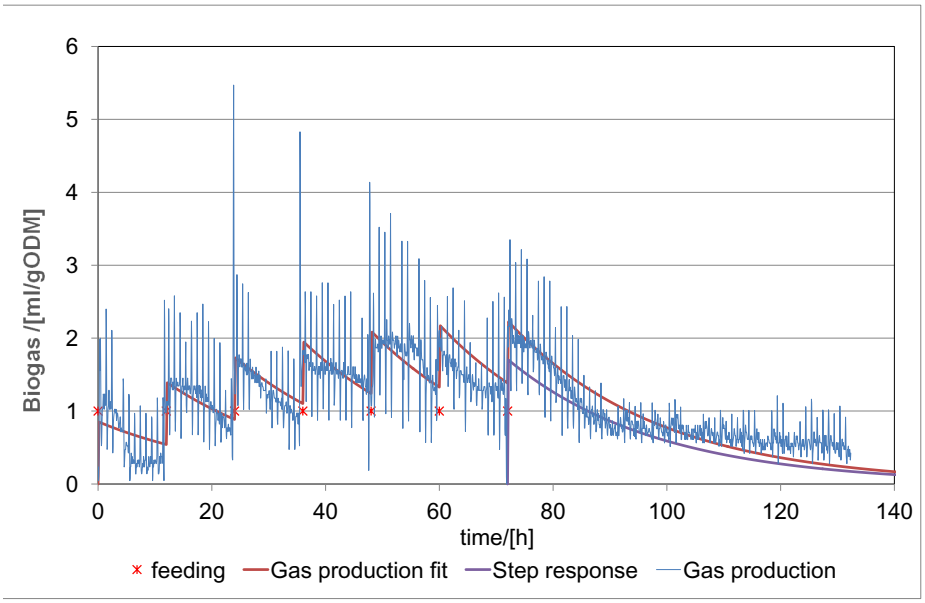


Figure 4.4.: Fit step response maize silage

In order to validate the results obtained, a similar feeding schedule as in Tab. 4.1 was applied in a second lab reactor. The reactor available for this measurement has a volume of 23 l with similar configuration to that in Fig. 3.3 on page 40. Feeding quantities were adjusted based on the lab results to obtain similar OLR. Inoculum and substrate for the lab reactor were obtained in the same biogas plant which is the subject of this study.

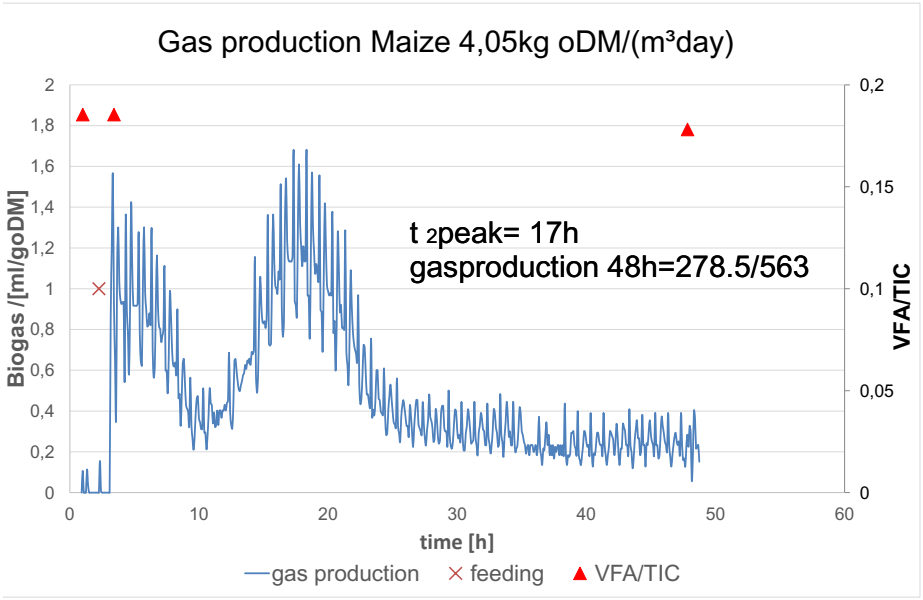
Samples were sent for characterization to an external lab, see Tab. A.1 positions #2 and #3 (Analysis for lab reactor 2). Inoculum and substrates for the lab digester were collected 1 week later. Substrate characteristics were assumed to be like the samples sent to an external lab, but due to the higher biogas production compared with lab reactor 1, the samples that had been preserved at 4°C were analyzed again. The preserved samples from lab reactor 2 had a higher dry matter content than was assumed, see Tab. A.1 position #5 (Analysis for lab reactor 2). As a result this

digester was exposed to a higher OLR. The feeding schedule with the corrected OLR is presented in Tab. 4.2.

OLR	4.05 $kg\,oDM/(m^3 \cdot day)$	5.3 $kg\,oDM/(m^3 \cdot day)$	5.3 $kg\,oDM/(m^3 \cdot day)$
HRT	104.5 d	80.1 d	12.16 d
feeding quantity	220 g maize silage	287 g maize silage	1890 g pig manure
feeding interval	Single feeding	Single feeding	Single feeding
starving time	144 h	140 h	48 h

Table 4.2.: Feeding schedule for lab reactor 2

Fig. 4.5 on the following page presents measurements for lab reactor 2 with different OLRs. Two biogas production peaks are present which are consistent with results obtained in the lab reactor 1. The time of the second peak in lab reactor 2 was different for both measurements. At a higher OLR the second peak is higher, which is consistent with the measurements in Lab reactor 1. Accumulated gas production in the first 48 hours is lower at a higher OLR. VFA/TIC values were in a stable range.



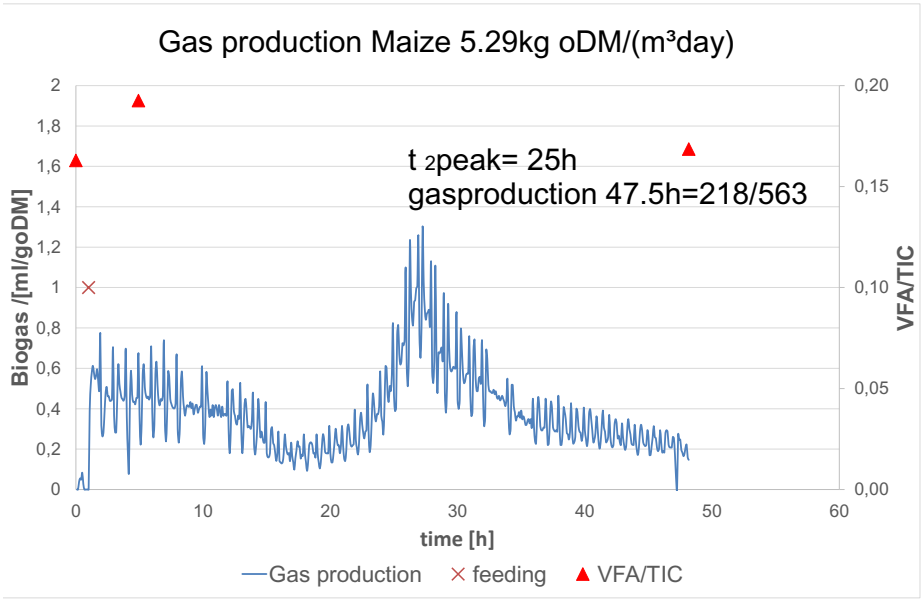


Figure 4.5.: Gas production measurements lab reactor 2 maize silage a)Single feeding $4.05 kg\, oDM/(m^3 \cdot day)$ b)Single feeding $5.3 kg\, oDM/(m^3 \cdot day)$

Lab reactor 2 reactor was fed with pig manure to determine the step response. It was intended to generate a single feeding with OLR like the commercial reactor, which implies a shorter retention time due to low organic content. Most of the biogas production was concentrated in the first 15 hours and gradually decrease after that, see Fig. 4.6.

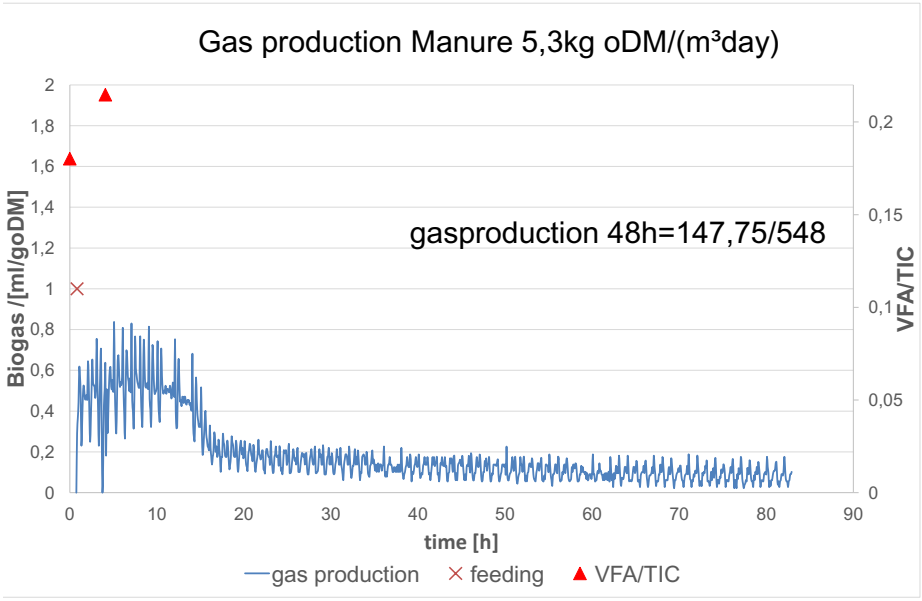


Figure 4.6.: Gas production measurements pig manure a)Single feeding $5{,}3kg\,oDM/(m^3 \cdot day)$

4.2. Online monitoring

4.2.1. Sampling parameters

In order to set the process parameters a series of measurements described in sec. 3.4.2 were developed. The aim of the analysis was to identify the configuration with the least standard deviation. In Fig. 4.7 on the next page, the results of the measurements are given for different subsample volumes and number of subsamples. Digester conditions were kept constant and there was no indication of a process disturbance during the measurement period. The lowest graphic presents the feeding and agitation schedule. It could be seen that the measured values for VFA and TIC varying up to 50% while the VFA/TIC ratio is almost constant. VFA/TIC stable results are characteristic of a stable biological process.

For each configuration the average, standard deviation and RSD (relative standard deviation) as well as maximum and minimum VFA/TIC relations are given, see Tab. 4.3. It can be seen that each configuration presents a low variation and average values are quite close to each other. The configuration with the largest sample volume and can be identified as it has the lowest variation of all the measurements.

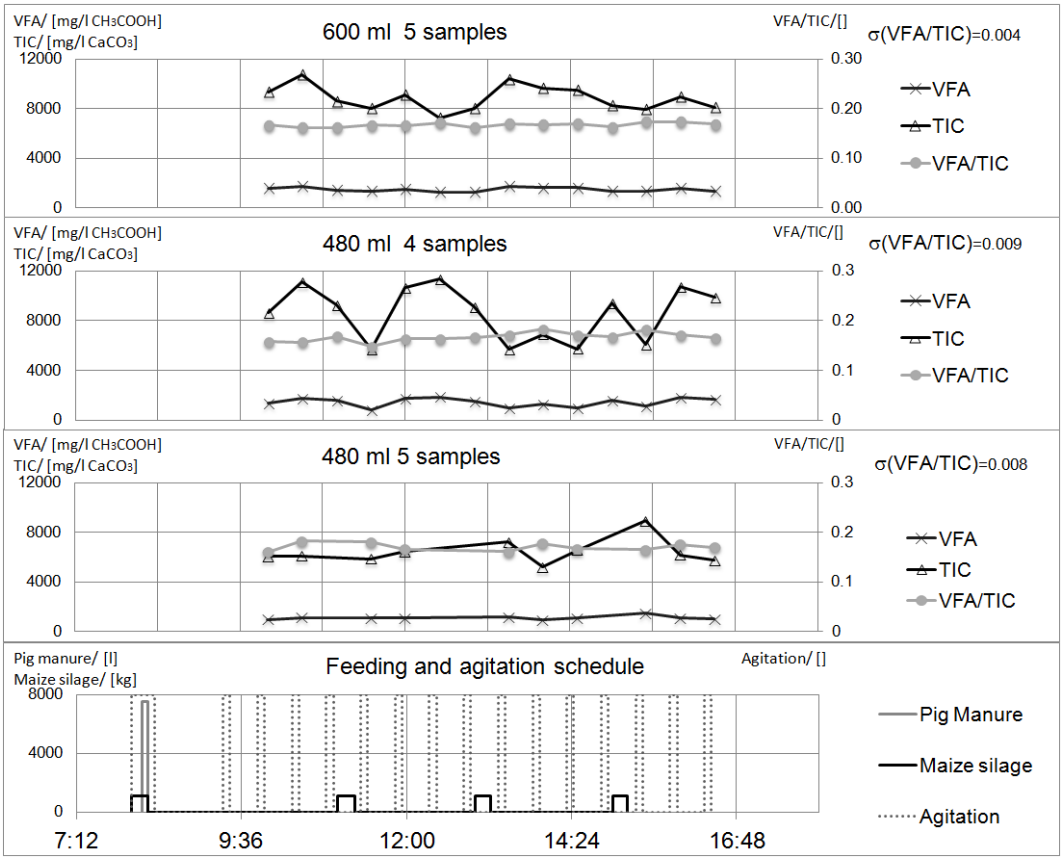


Figure 4.7.: Configurations comparison sampling parameters. Lowest graphic presents corresponding feeding and agitation schedule

Configuration	σ	$\overline{VFA/TIC}$	$RSD = \frac{\sigma}{\overline{VFA/TIC}}$	Max VFA/TIC	Min VFA/TIC
5 subsamples of 120 ml	0.004	0.167	2.4%	0.173	0.162
4 subsamples of 120 ml	0.009	0.167	5.5%	0.183	0.148
5 subsamples of 96 ml	0.008	0.170	4.7%	0.183	0.160

Table 4.3.: Configuration comparison VFA/TIC parameters.

4.2.2. Measurements in the commercial plant

The biogas plant studied, described in sec. 3.1, has been operating for 7 years without any serious biological process imbalance (based on the information supplied by the operator). In the two-year supervision period of this work only one disturbance of the biological process occurred and happened at continuous feeding conditions. Detailed description of this event is presented in sec. 4.2.2.3.

The online monitoring system developed and calibrated in this work was used to detect whether changes in feeding affects the biological process. A series of measurements were done at normal operating conditions (continuous feeding) and with a modified feeding program (feeding on demand).

During normal operating conditions VFA/TIC measurements did not present large variations during the almost two years of measurements. Three feeding transitions are presented Fig. 4.8, Fig. 4.9 and Fig. 4.10.

4.2.2.1. First feeding transition.

After a period of two months without large variations of the VFA/TIC ratio it was decided to implement the first feeding transition. Before modification the feeding was kept constant with the plant operating at its design parameters of $OLR = 2.65 kg\, oDM/(m^3 \cdot day)$ and $C/N = 25.68$.

The feeding program was modified on 15.08.2017 from feeding almost every 2 hours to every 12 hours, see Fig. 4.8 on the following page. This modification was based on the findings in [13, 161] and lab results (see Fig. 4.3 on page 83), as most of the gas yield dynamic changes were found in the first 12 hours. The idea behind this was to increase the biogas production to match the two electricity cost peaks presented in the yearly average electricity prices from the Day Ahead Auction of the EPEX SPOT SE [1].

This transition was done with the original configuration of the gas storage, the Baur "calming system" (see sec. 3.5) and gas management (see sec. 3.5.3) were not yet implemented.

It can be observed that changing from two hourly feeding of Maize silage (12 ton/day) to twice a day did not affect the biological process. Pig manure was fed once a day, its quantity and feeding time were constant due to operational reasons.

VFA/TIC were measured 4 times a day (before and after the two feeding times) and values remained relatively constant during both continuous and variable feedings.

[1] The EPEX SPOT operates short term trading for Power in Germany, France, Austria and Switzerland

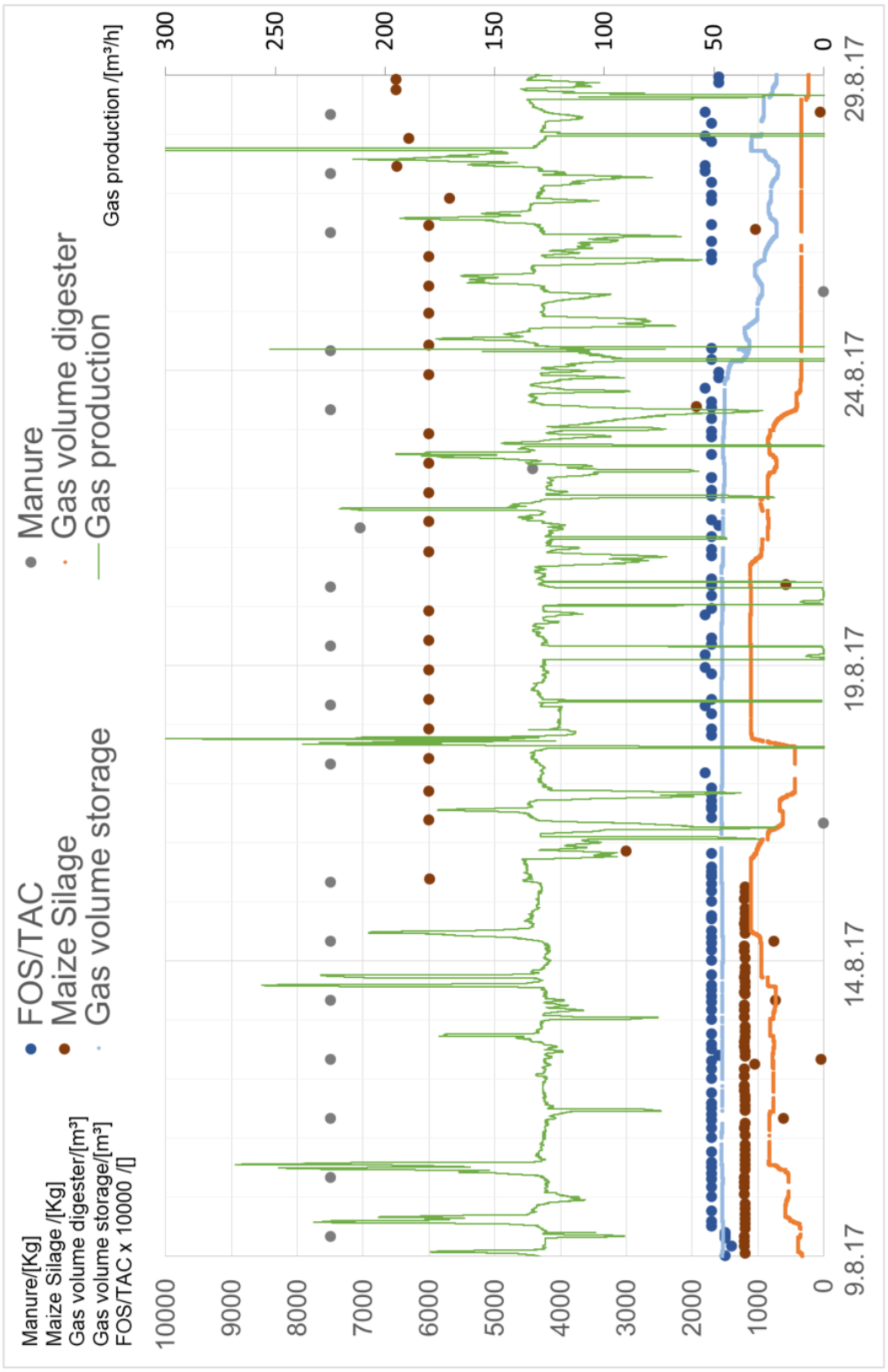


Figure 4.8.: Transition continuous vs variable feeding. Measurement done without gas storage modification

4.2.2.2. Second Feeding transition

The feeding program was modified again on the 13.11.2017 from two feedings per day to only one, see Fig. 4.9 on the following page. Measurements were then collected after installing the Baur calming system; however, the gas management system was not yet implemented, see sec. 3.5.1.

Gas production calculation to single feedings vary with different digester and storage gas fill levels. From 5.11.2017 to 8.11.2017, gas production with an empty digester and half-filled storage was lower than the period from 8.11.2017 to 13.11 2017, feeding with similar substrate quantities. In this period, with a larger gas volume, gas production is like previous to lab measurements (see Fig. 4.3) and as expected from feeding on demand. Daily gas production in this period was not constant which lead us to measure the maize dry matter content to determine if the variation is coming from the substrate. We found that dry matter content is substantially variable between feeds.

Energy content extrapolations based on dry matter content presents large variations between 14.11.2017 and 21.11.2017, see Tab. A.1.The inconsistency within this period can be attributed to a substrate change between maize silages from two different years.

The feeding program was modified on 13.11.2017 from two feedings per day to a single feeding per day. VFA/TIC values remained constant showing no effect on the biogas production.

System response from 13.11.2017 to 17.11.2017 with an empty digester and a full storage tank was not as expected. However, once the digester was filled the system then performed the expected step response. Step response changed while filling level varied.

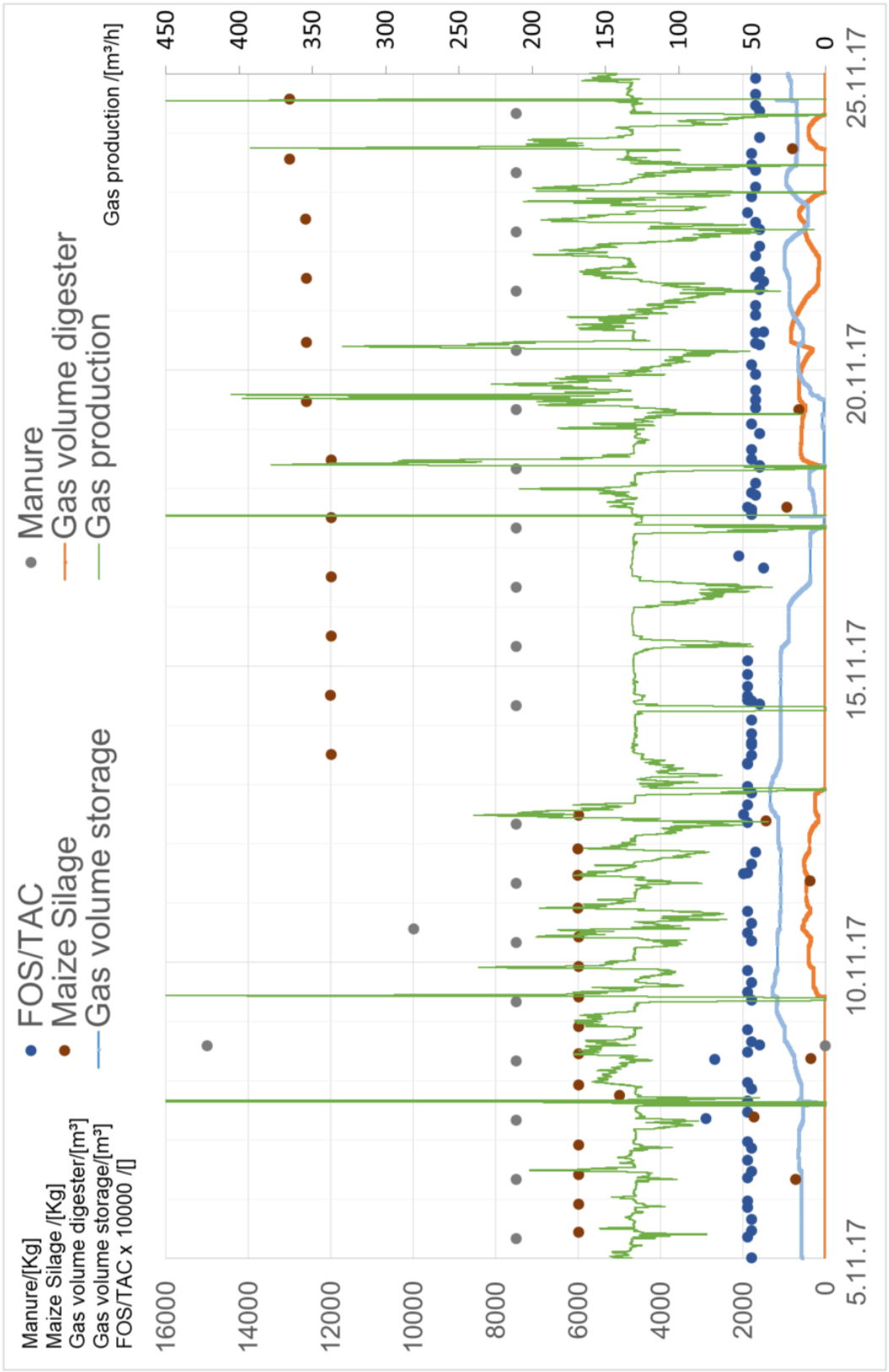


Figure 4.9.: Transition continuous vs variable feeding. Measurement done after installation of Baur "calming system"

4.2.2.3. Third feeding transition

A third feeding transition was planned after gas storage management was commissioned to improve gas volume measurements. As with previous transitions the biogas plant was operating at its design parameters of $OLR = 2.65 kg\, oDM/(m^3 \cdot day)$ and $C/N = 25.68$ and the heating and agitation systems were working correctly.

Before feeding modification, online monitoring was able to detect a process imbalance. Data from three months of online monitoring are presented in Fig. 4.10 on the next page. This period includes the process disturbance, recovery period and the change from constant feeding to feeding on demand during which online monitoring was in place to detect whether feeding modification negatively affects the biological process. Methane concentration was measured at the gas pipe just before the CHP unit using an Extox IMC 4D with an infrared absorption transmitter.

Maize silage dry matter was measured daily (see Tab. A.1) as as part of the original plan before the feeding program would be changed, but due to the system imbalance during this period it was necessary to postpone the feeding modification. No changes in the substrate were found to explain the process disturbance.

Lab results during the imbalance period are presented in Tab. 4.4. This also presents trace element concentrations from the last 2 years. The lowest Cobalt concentration is found on 12.03.2018.

Date	16.08.2016	07.06.2017	12.03.2018	26.03.2018	25.04.2018
Dry matter/[%]	6.6	8.7	7.4		7
Acetic acid equivalent/[g/kg]	0.39		2.32	5.41	0.32
Ni/[mg/kg]	0.46	0.423	0.648		0.669
Co/[mg/kg]	0.20	0.148	0.143		0.236
Mo/[mg/kg]	0.37	0.416	0.402		0.432
Se/[mg/kg]	0.17	0.137	0.140		0.144

Table 4.4.: Lab results biological supervision including trace elements concentration from the last 2 years. Dry matter method (VDLUFA I, A 2.1.1; 1991 (mod.)), Acetic acid equivalent method (VDLUFA II, 3.2.6, 1995), Ni, Co, Mo, Se method (DIN EN ISO 17294-2; 2005-02 (mod.))

The first variation of VFA/TIC was detected on 09.03.2018, which initially was assumed to be failure in the online system, due to the characteristically stable operation of the plant. To investigate this problem, gas analysis was put in operation on 09.03.2018, where CH4 concentration was found to be within a normal range, so no special attention was given to the VFA/TIC increase.

VFA/TIC values continue to increase in subsequent days and as the reason for the imbalance was not known, a sample was taken on 12.03.2018 to verify the measurements of the online monitoring and measure the concentration of trace elements.

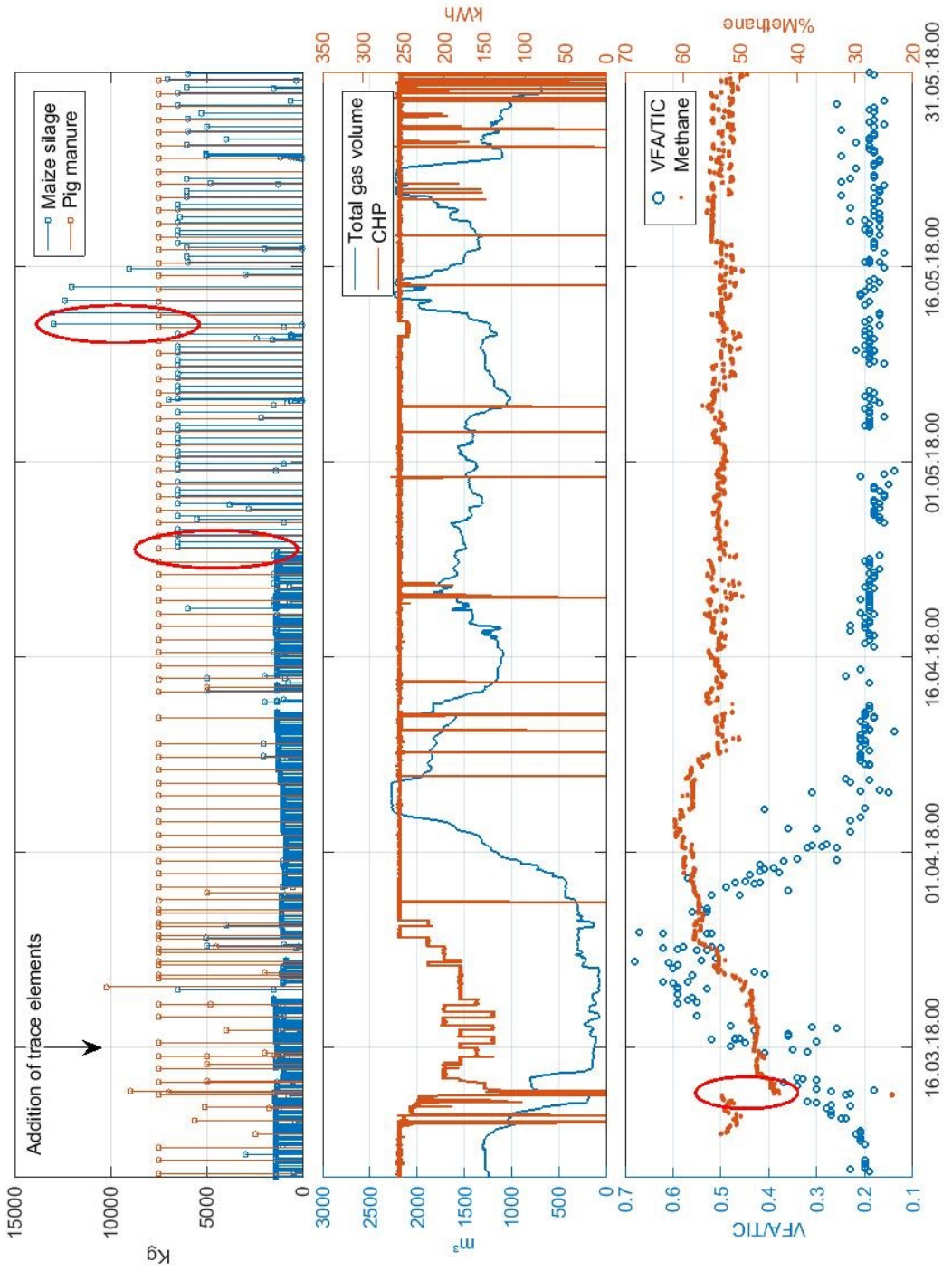


Figure 4.10.: Three months online monitoring. On the abscissa time is given in days and on the ordinate the following aspects are given. Above: presents the digester feeding. Two feeding transition of maize silage can be identified from 1300kg almost every 2 hours to 6500 kg every 12 hours and later 13000kg once a day. Middle: presents gas storage volume and CHP electrical generation. Generated power was reduced due to the low gas storage levels. Below: presents results of online monitoring and methane content. Process disturbance can be identified by the increase of the VFA/TIC. Calibration of the gas analyzer is marked showing a difference in the methane content from 53 % to 45%

On the same day the plant owner agreed to reduce feeding because the gas storage was empty to allow for the system to recover. The lab results arrived on 13.03.2018 showing a significant increase in acetic acid confirming the results obtained by the online monitoring. Calibration of the gas analyzer was performed on 13.03.2018 where methane concentrations were recorded at 45%. This reduction of methane production indicated a process imbalance due to higher CO_2 production and reduced conversion of intermediate metabolites into CH_4.

After a short recovery of the gas production from 13.03.2018 to 14.03.2018 the plant owner decided to increase feeding to produce as much power as possible. Contrary to our recommendations he also fed Corn-Cob-Mix, which is known to give faster biogas production, but with a higher organic content than maize.

On 16.03.2018 a solution containing Co and Ni (800 gr $CoCl_2.6H_2O$+$NiCl_2.6H_2O$ at 24.7% weight in Co and Ni) was added, as it is known that agricultural plants normally have a deficiency of both. Trace element analysis was ready on the 22.03.2018, showing slightly lowered levels of cobalt.

The biogas plant was fed with a similar quantity as before the process imbalance occurred but produced a lower gas yield, meanwhile the VFA/TIC value continued to increase. The plant owner resisted reducing feeding despite our recommendation. Pig manure feed was increased with the aim of increasing buffer capacity, due to its high nitrogen content, generating a short-term reduction of VFA/TIC.

On 20.03.2018 the VFA/TIC level stabilized at a high level, and methane concentration started to rise, indicating an improvement of the biological process. Manure quantity was doubled in order to keep the system stable.

A second sample was sent to the lab on 26.03.2018 to verify the online measurement. Lab results confirmed online results showing a large accumulation of VFA.

After the 27.03.2018 VFA/TIC started to decrease with an increase of methane concentration up to 60 %, atypical for this kind of plant, clearly signaled by the conversion of acetic acid into methane. The gas yield increased and feeding was reduced because gas storage had reached its maximum. VFA/TIC returned to a normal level of 0.2 as did methane concentration of 52%.

On 25.04.2018 a control sample was taken confirming the recovery of the system and the validity of the values shown by online monitoring which had remained constant since 9.04.2018.

The feeding program was modified again on 23.04.2018 from feeding almost every 2 hours to every 12. As the system remained stable, the feeding program was then modified on 11.05.2018 to one feeding per day with the aim of concentrating the biogas production to match peaks in price.

As the engine in the test plant operates at constant power, a match between gas production and consumption was not achieved. For that reason, gas storage capacity reached high levels (over 90%) and the feeding had to be modified again on 15.05.2018 to avoid gas loss.

4.3. Gas volume measurements

4.3.1. Operational range gas storage.

In order to determine the maximum allowed gas storage operating limit a series of measurements in the research plant were done, see Fig. 4.11 on this page. These took place before the Baur calming system installation, see Fig. 3.13 on page 66. According to the gas level two operating ranges can be identified:

- Membranes touching: gas temperature presents large variations. Gas pressure at its maximum level
- Membranes separated: gas temperature follows ambient temperature.

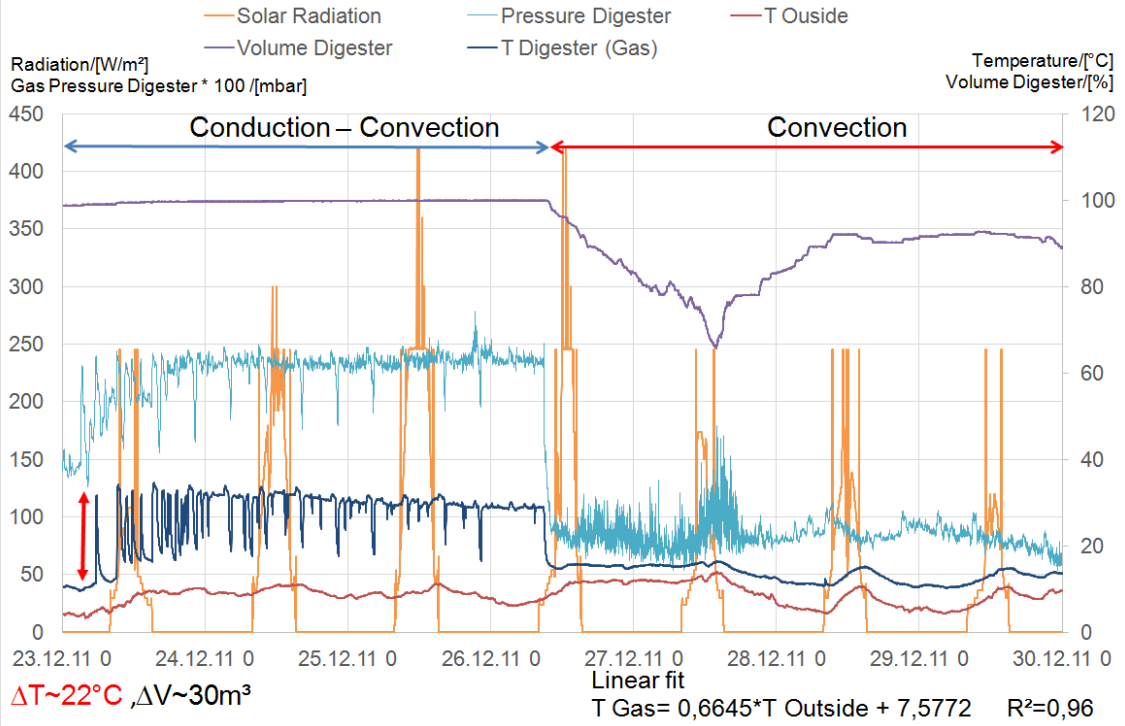


Figure 4.11.: Gas volume variation by temperature and solar radiation for $22m$ Digester. This figure was obtained from values taken in the digester before the installation of the Baur "calming system".

4.3.2. Operational conditions generated by the gas management system

A series of measurements were made on the gas storage system in the digester and storage using the gas management control system developed in this work, see

sec. 3.5.3. Gas was moved between the digester and storage by the changing the revolutions per min rpm of the fan.

The objective of the measurements is to verify the selection of rpm_{D-MIN} and rpm_{S-MIN} in order to guarantee a minimum pressure and volume to keep the system stable at different filling levels. This procedure will also help us understand the effect of solar radiation and ambient temperature on the gas storage.

Installed fans in the digester and digestates storage are the same model. Both rpm_{D-MIN} and rpm_{S-MIN} were fixed initially to $2503/min$ but after a series of preliminary measurements (not presented) it was quickly noticed that rpm_{S-MIN} needed to be further reduced to $2345/min$ in order to generate the pressure gradient towards the storage tank $P_{gS} < P_{gD}$, see Fig. 3.16. This indicates that the system curve of the digestates storage tank has a higher loss than the digester which is expected due to its larger dimensions.

In Fig. 4.12 on page 99, 3 changes in the operation of the digester are marked with 1, 2 and 3

1. Move gas to storage. Reduce fan rpm in storage to its minimum and keep rpm in digester at nominal capacity. Gas pressure in digester is higher (green line) and gas moves to storage. In about 4 hours storage attains maximum value of 75% as there is no more gas available. Fan volume presents large variations with oscillations of $100m^3/h$.

2. Move gas to digester. Reduce rpm in digester to its minimum and keep rpm in storage at nominal capacity. About six hours are needed to reverse fill levels. This information gives us the maximum required time to empty a tank where maintenance is required (open gas storage membranes). Delivered fan volume is constant at different filling levels until the digester reaches a maximum fill, at this point a mechanical blockage of the air inlet takes place and no air is pumped between the membranes because the air inlet is covered by the gas retaining membrane.

3. Normal operation. In this case the system tries to keep fill levels of both tanks the same, $|VN_D - VN_S| \leq 5\%$. At the beginning digester gas storage volume remains constant while pumped air volume increases. This indicates a measurement delay which will affect the gas production calculation.

In Fig. 4.12, in which the above operations are marked 1 2 and 3, the equilibrium between the gas pressure in both storages (P_{gD} , P_{gS}) and air pressure of the supporting fans (P_{aD} , P_{aS}) can be observed. For example when the gas is moved to digester (marked 2) P_{aD} is reduced, decreasing the P_{gD} but because this digester is connected to the storage tank P_{gD} and P_{gS} are in the same range. Once the digester is full P_{gD} increases as there is no more volume available, also increasing P_{gS}. P_{aD} decreases further as the air inlet is blocked and the air leaves the system at the pressure regulating valve located on top of the supporting fan, see Fig. 3.18.

Another example of how one supporting fan can affect the pressure of both gas storages (P_{gD} , P_{gS}) was observed on 18.4.18 at 0 h. In this case the control system, in order to keep the same gas storage levels in digester and storage, reduced the digester fan rpm, reducing P_{aD}. This reduction generated a drop in both pressures (P_{gD} , P_{gS}) producing a lower gas pressure in the digester, necessitating movement of gas into the digester.

The same operation mode is presented in the storage tank, see Fig. 4.13 on page 100.

Measurements of temperature effects in the digester and storage tank are presented in Fig. 4.14 on page 101 and Fig. 4.15 on page 102. In both tanks, gas temperature follows ambient temperature and the offset between both temperatures is higher in the digester than in the storage due to the heating in the digester. There is a delay between solar radiation and the increase of the fan pumped air temperature measured at the pressure regulating valve (T Digester pump air and T storage pump air), see Fig. 3.18 on page 71. Increase of fan pumped air temperature is accompanied by a decrease of the fan pumped air volume (fan volume digester and fan volume storage).

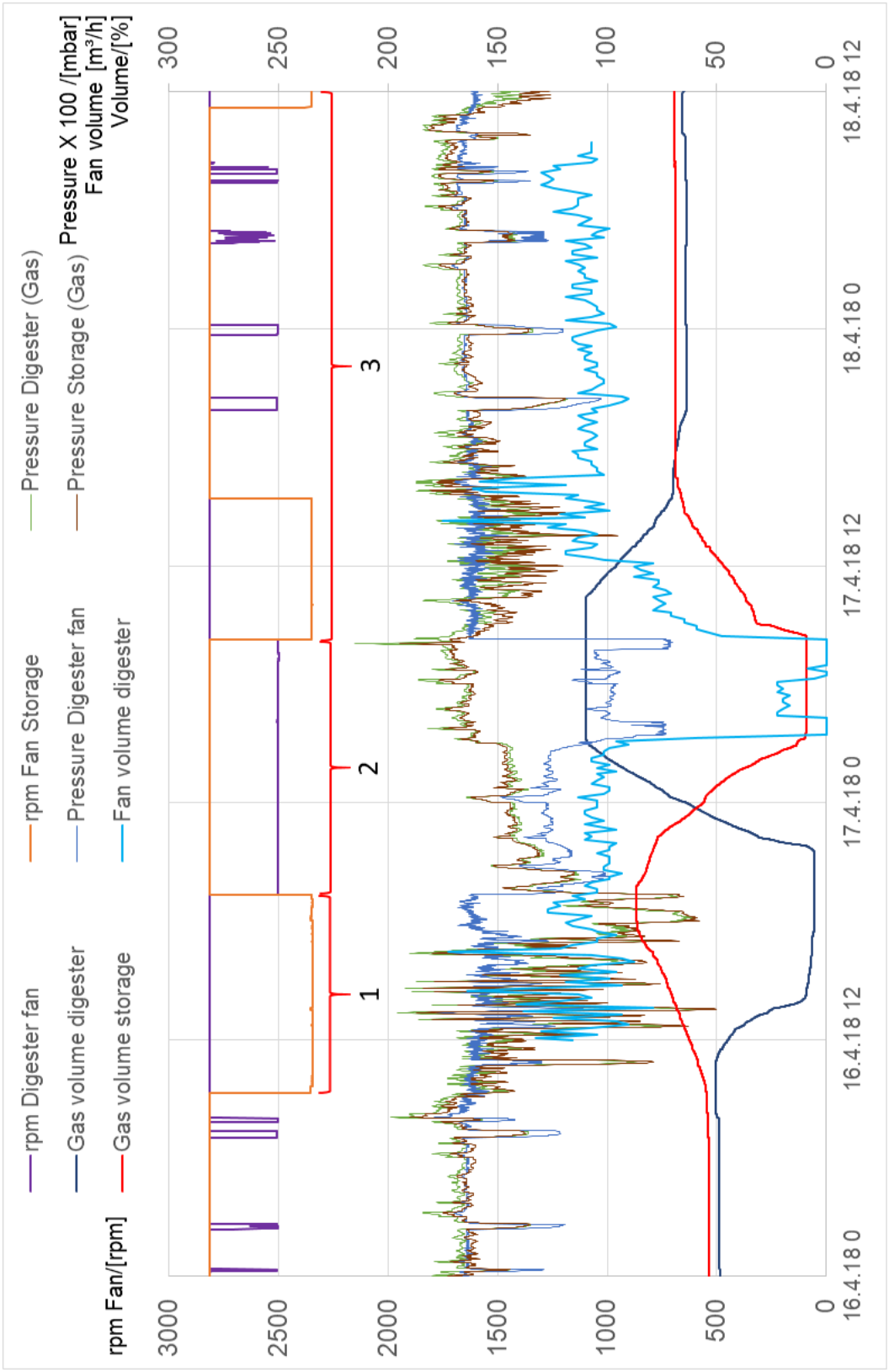


Figure 4.12.: Measurements volume fan digester

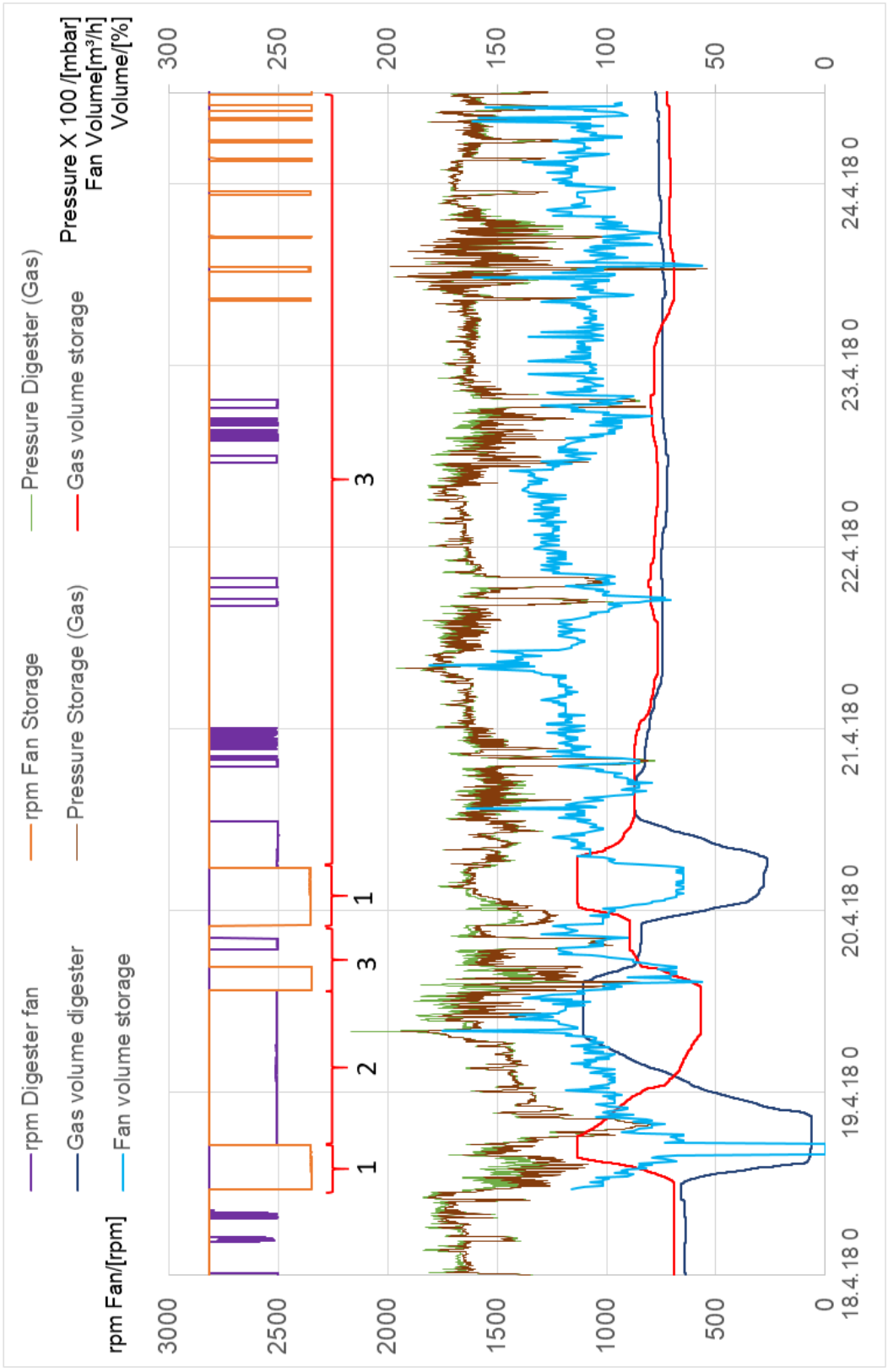


Figure 4.13.: Measurements volume fan storage

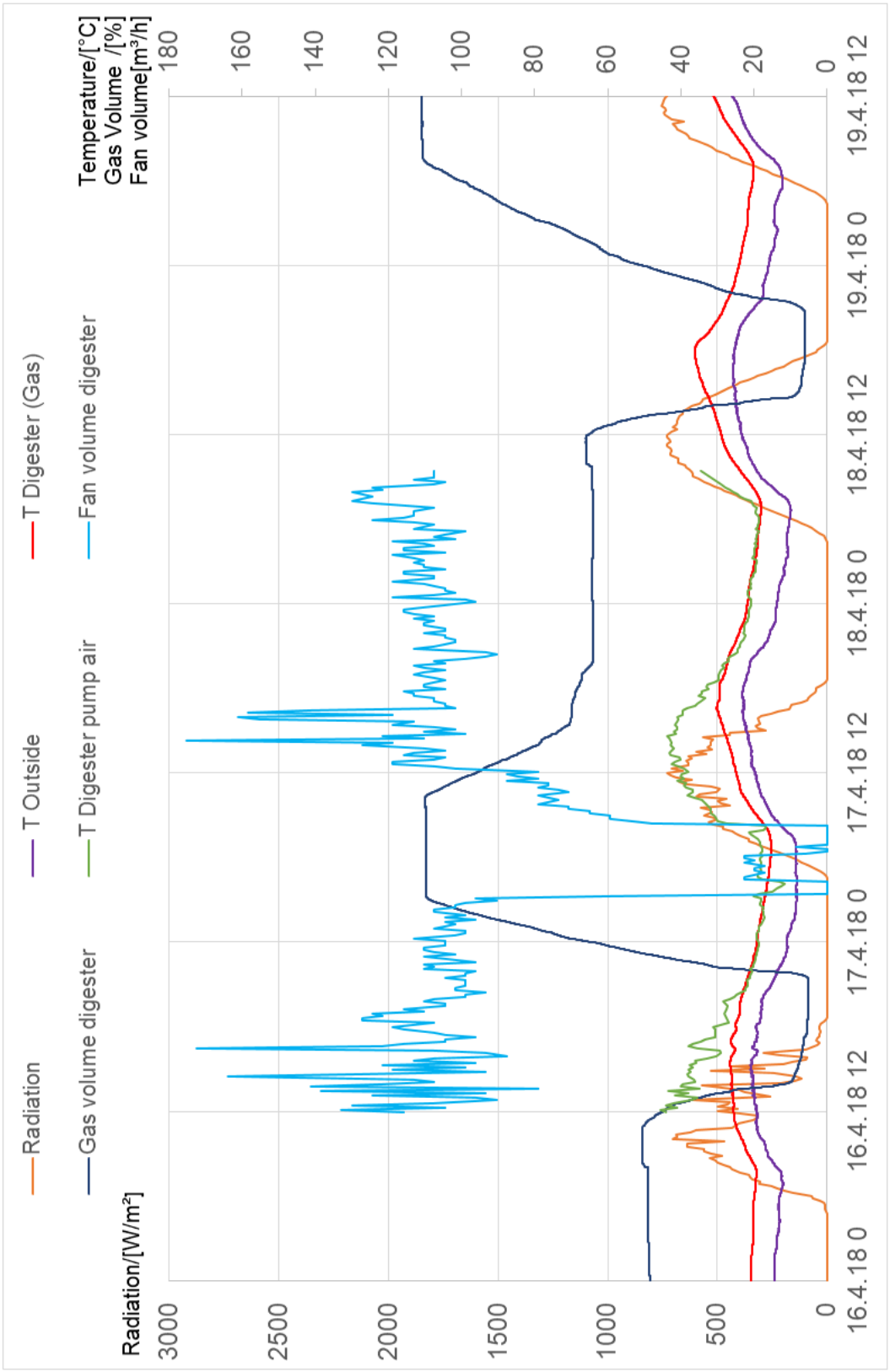


Figure 4.14.: Temperature effect in digester

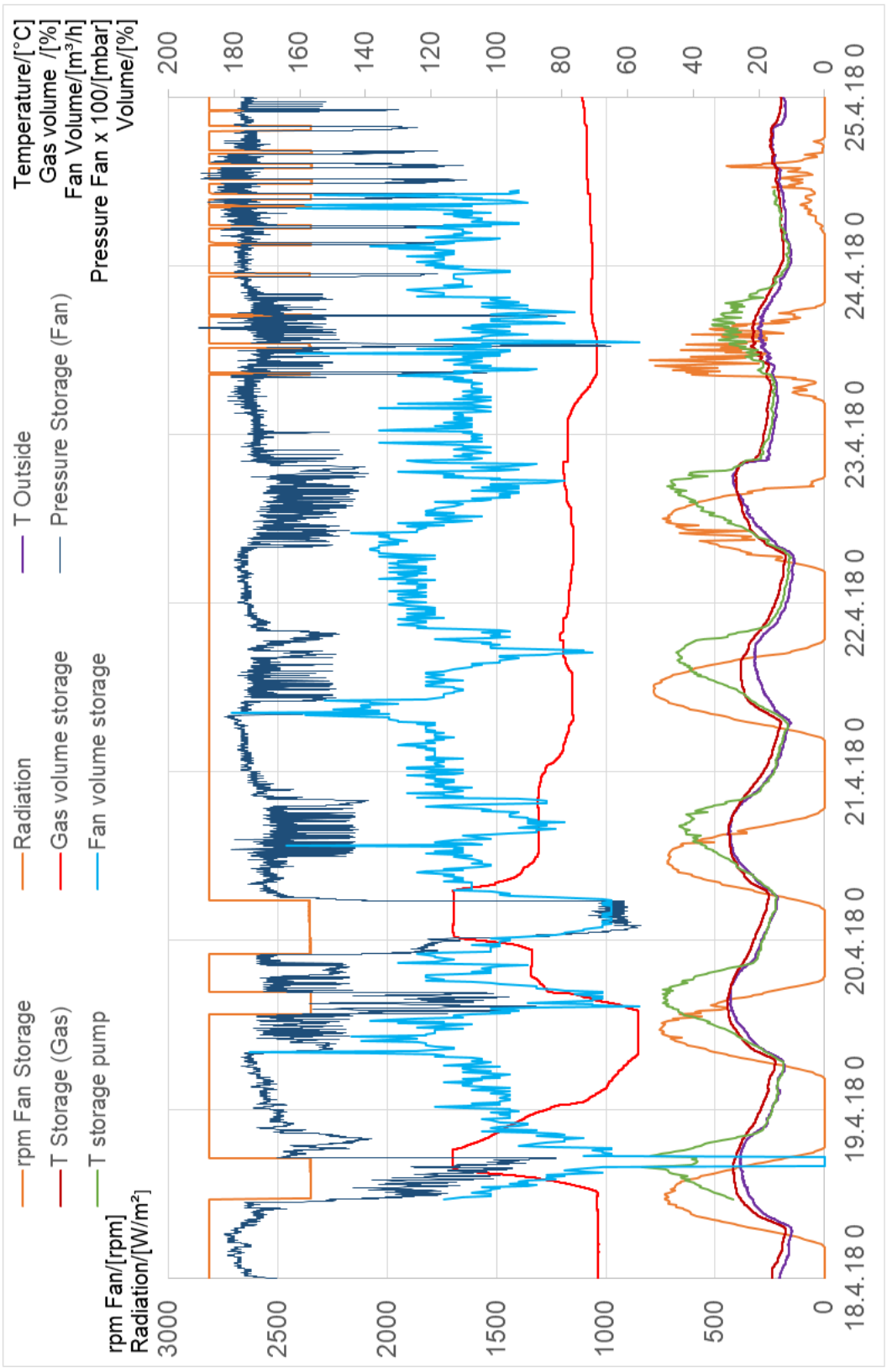


Figure 4.15.: Temperature effect in storage

4.3.3. Dependency of gas storage levels in calculation of gas production.

A comparison to determine whether the gas production calculation can be improved with use of the gas management system was developed, see Fig. 4.16. Gas management was in automatic operation; from 16.4.2018 to 20.4.2018 volume levels were manually modified and after this time returned again to automatic operation. A comparison is made between calculated gas production when both tanks are at the same level, controlled by the gas management, and when the gas levels varied.

Volume variations were manually generated by decreasing fan rpm on one tank and vice-versa. Gas was moved between the digester and storage leaving the feeding program constant. If the variation in volume does not depend on membrane levels, the calculated volumetric production of gas should be the same as that obtained when both membranes are at the same level. Fig. 4.16 shows that Max levels of gas in the digester and storage are higher than 100 %. This is because the 100% volume was fixed at the equivalent rope length $\triangle r = 1.635m$, see Fig. 3.11. This digester at 100 % fill is equivalent to a volume of 774 m^3 obtained for a spherical cap. Membrane shape for a larger $\triangle r$ will not be spherical as the membrane was manufactured to be conical, which introduces an additional error source in the calculation, as the volume is determined assuming a spherical cap. This makes the estimation of the desired operating range difficult.

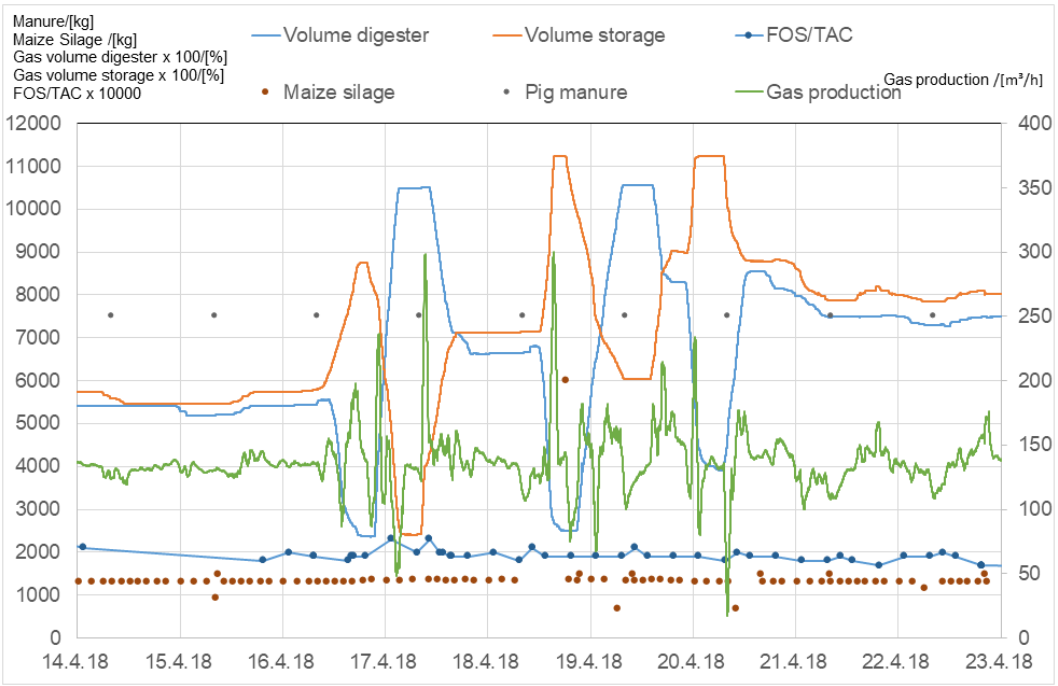


Figure 4.16.: Gas production at different gas storage levels

4.4. Model Validation

A series of measurements to determine the step response to a single feeding were undertaken at the commercial biogas plant after improving the gas production calculation by installing the Baur calming and gas management systems.

The feeding program was modified on 23.04.2018 to determine maize silage step response. Fig. 4.17 on the next page presents the transition from continuous feeding to two feedings a day. Feeding transitions did not affect the biological process, similar results were found in previous measured feeding transitions (Fig. 4.8 and Fig. 4.9).

The red line corresponds to the gas production calculated by the model using the step response for maize silage, see equation 4.1 and the measured step response for pig manure, see 4.1. Due to CHP gas flow meter calibration failure the model prediction was normalized with the average measured production to avoid the generated offset.

Fig. 4.18 on page 106 presents the calculated process parameters for 6 weeks operation.

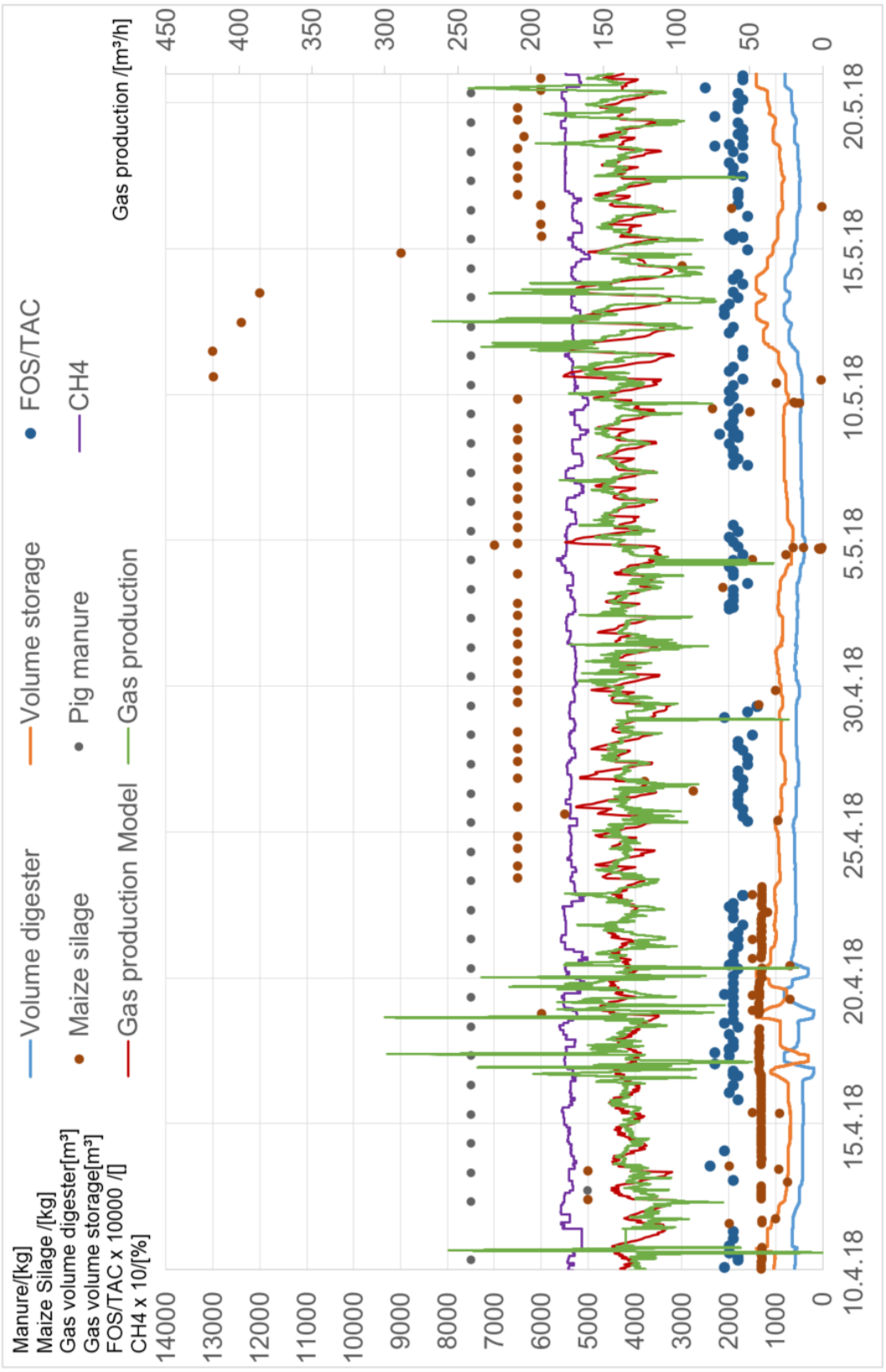


Figure 4.17.: Gas production vs model estimation for 6 weeks comparing transition between continuous and variable feeding. (After installation of Baur "Calming system" and gas management)

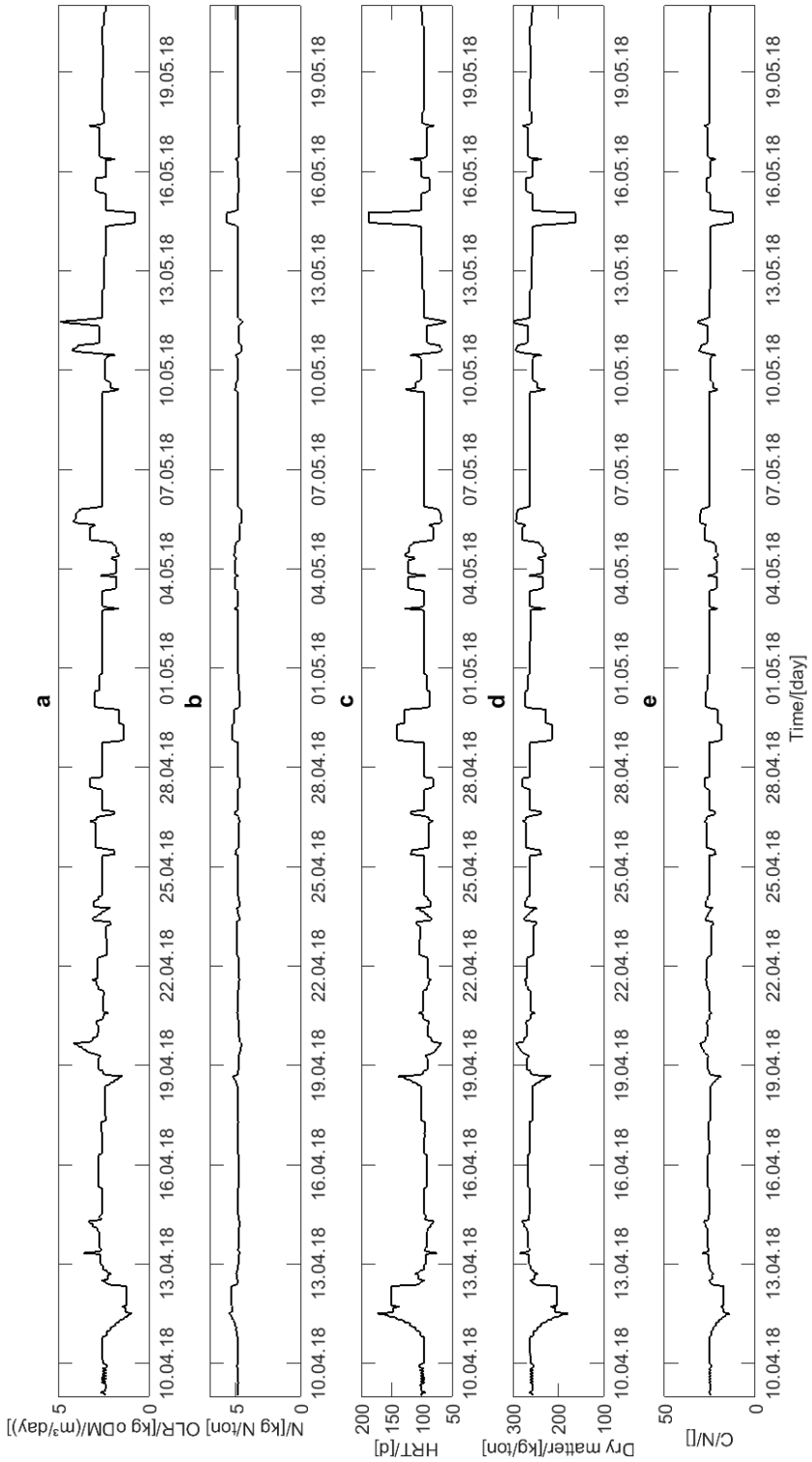


Figure 4.18.: Process parameters of feeding program calibration a) organic loading rate; b) Nitrogen content; c) Hydraulic residence time; d) Dry matter e) C/N

4.4.1. Feeding model application

A feeding program using the optimization algorithm described in sec. 3.2.2 was calculated for the plant under testing to demonstrate its potential. Step response obtained from the lab reactor was used for the algorithm as direct measurement of step response of the biogas plant was not possible.

The following conditions were imposed on the optimization algorithm:

- Installed electrical capacity 250 kW
- Possible expansion by a further 250 kW engine.
- Minimum electrical power 125 kW (The biogas plant has a contract to deliver a minimum amount of heat)
- Maximum Power 250 + 250 kW = 500kW
- Average Load Power = 250 kW
- Maximum gas storage allowed was fixed at 90% of the capacity of both digester and storage. Max gas storage = 2038*0.9 = 1834 m^3.
- Minimum gas storage is fixed at 20%. Min gas storage = 406 m^3
- Maximum gas storage to provide grid services. This example simulates the situation in which the biogas plant delivers a negative minute reserve which means that maximum filling volume was limited to 1500 m^3 so that the net operator can remotely shut down the engine and the biogas plant has an additional storage to avoid flaring the excess gas while not generating.
- Minimum gas storage to provide grid services. The example of a positive minute reserve was not considered in the algorithm. Min gas storage level could be increased to consider this situation which would involve raising the minimum gas storage level from 406 m^3.
- Total available gas volume (TAGV)= Max gas storage - Min gas storage = 1428 m^3
- A solid feeder, capacity up to 5 Mg per hour. $lbsolids = 5$
- The pump which delivers manure has a 50 m^3/ h feed capacity. $lbliquids = 50$
- Process parameter limits were as described in sec. 3.2.3.
- Maize silage with 36.7% DM, biogas yield= 200.42 m^3/Mg and Pig manure 8.9% DM, biogas yield = 26.71 m^3/Mg. With these substrates 13.5 Mg of maize silage and 7.5 m^3 of pig manure are required to achieve 250 kW average per day.

4.4.2. Load profile

In principle any load profile is possible but in order to evaluate the performance of the feeding model a load profile which maximizes economic revenue was selected.

Load profile was estimated based on the yearly average electricity prices for year 2014 from the Day Ahead Auction of the EPEX SPOT SE. It was noted that the prices had two peaks during working days, and lower price levels during weekends.

The biogas plant optimizes profit when operating at maximum capacity (500 kW) during peak prices for seven hours a day (see Fig. 4.19), and the remaining amount of time including weekends at a lower capacity. Load profile was obtained after a linear optimization of the revenues having as a restriction a minimum power of 125 kWh[2]., a maximum power 500 kWh in the weekdays and in the weekends operating a minimum power. The total generated power in average over fourteen days including the weekends was 250 kW. This is required in order to establish a fair comparison between both feeding programs: constant feeding vs feeding on demand.

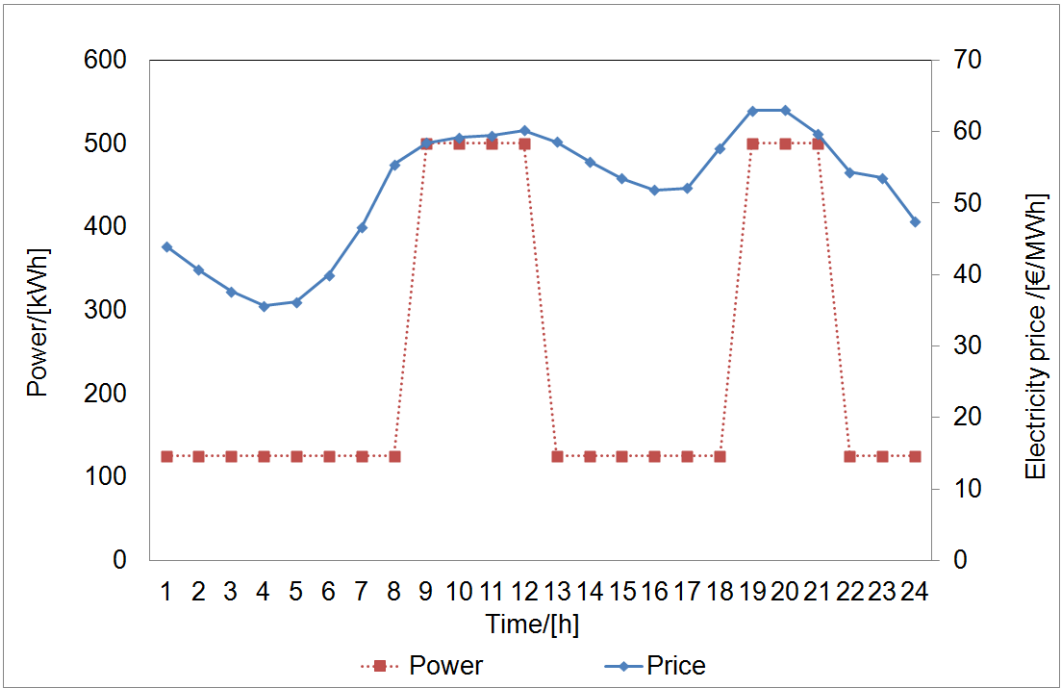


Figure 4.19.: Load profile for a week day. Dotted line represents the load profile with maximum revenue. Continuous line shows the yearly average electricity prices from the Day Ahead Auction of the EPEX SPOT SE.

4.4.3. Constant feeding vs Feeding on demand

Fig. 4.20 shows a comparison of the equivalent power generated by the biogas production and the resultant gas storage level with both feeding scenarios. The equivalent power is calculated as the product of the methane yield times the engine electrical efficiency.

[2]It was assumed for this calculation that the engine efficiency does not change with power output

The difference between the required load and the equivalent power generated by the biogas production must be covered by the gas storage. Fig. 4.20a on the next page shows the biogas production equivalent in power after a constant feeding, (blue line) and the required load profile, (red line). As was expected power production is almost uniform.

Fig. 4.20b, presents the resultant gas storage. In this case the biogas plant will not be able to deliver the requested load profile as a larger gas storage capacity is needed. The required gas storage capacity to deliver the load is $1634.6m^3$, which is calculated as the difference of the maximum and minimum gas storage. The required capacity exceeds the total available gas volume of $1428m^3$. This means that even at a higher initial gas storage level and without grid network service restriction (max filling level $1500m^3$) the plant can not deliver the required profile.

The results obtained with an optimized feeding program are presented in Fig. 4.20c and Fig. 4.20d. It can be observed that production tries to fit with the required load. During weekends (from hour 120 to 144) biogas production is minimized. Optimized feeding keeps the gas storage levels in the required range, reducing the gas storage capacity required to deliver the load to 1074.1 m^3.

The feeding program for both scenarios is presented in Fig. 4.21 on page 111. Fig. 4.21a corresponds to continuous feeding and Fig. 4.21b to the feeding on demand scenario. In Fig. 4.21b feeding is characterized by two feedings per day like the feeding program implemented in sec. 4.4. Daily feeding quantity increased up to $18.9Mg$ per day having a maximum $OLR = 4kg\,oDM/(m^3 \cdot day)$ and later is reduced to $12.2Mg$ with a minimum of $OLR = 2kg\,oDM/(m^3 \cdot day)$.

In feeding on demand process parameters are kept between the limits defined in sec. 3.2.3. Process parameters for this scenario are presented in Fig. 4.22 on page 112 and are characterized by higher organic load followed by a reduction to the minimum.

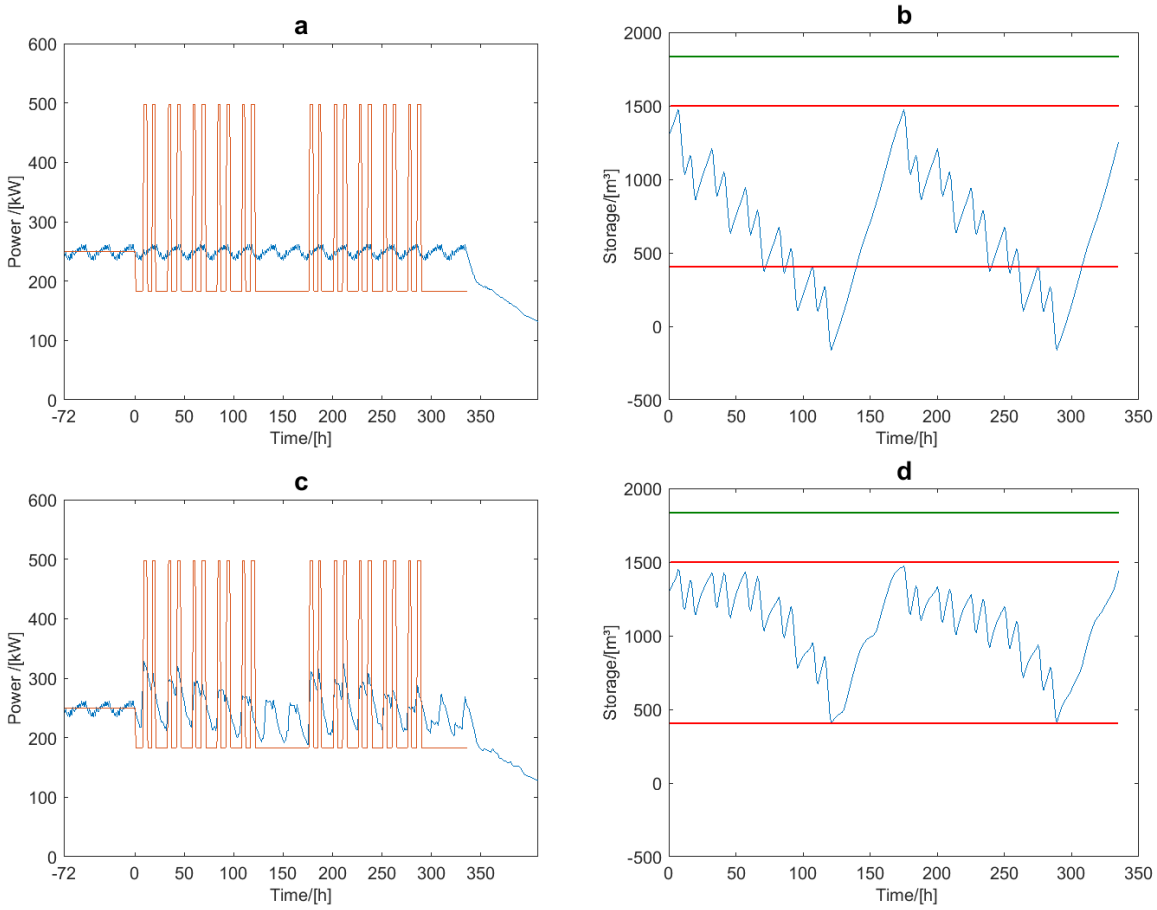


Figure 4.20.: a) Power production calculated as gas equivalent in a constant feeding program. c) Power production calculated as gas equivalent in feeding on demand. Red lines represent the required load and blue lines the power production equivalent to the gas production in each scenario b) Gas storage in constant feeding. d) Gas storage in feeding on demand. Upper green lines represent the maximum gas storage levels. Upper and lower red lines are the imposed storage volume range, (see sec. 3.2.3), to allow the operator to deliver balancing power

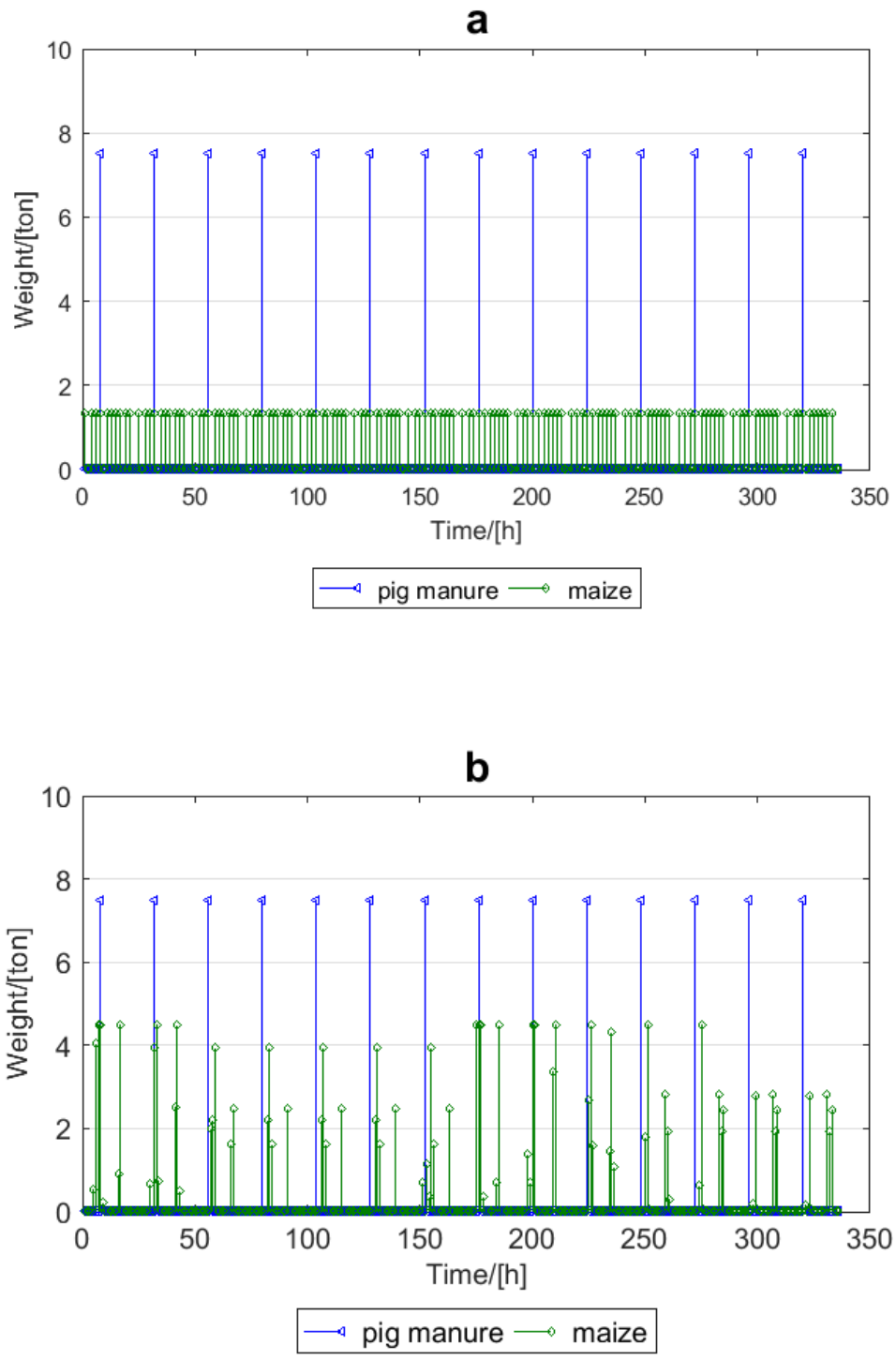


Figure 4.21.: a) Constant feeding program; b) Feeding on demand program

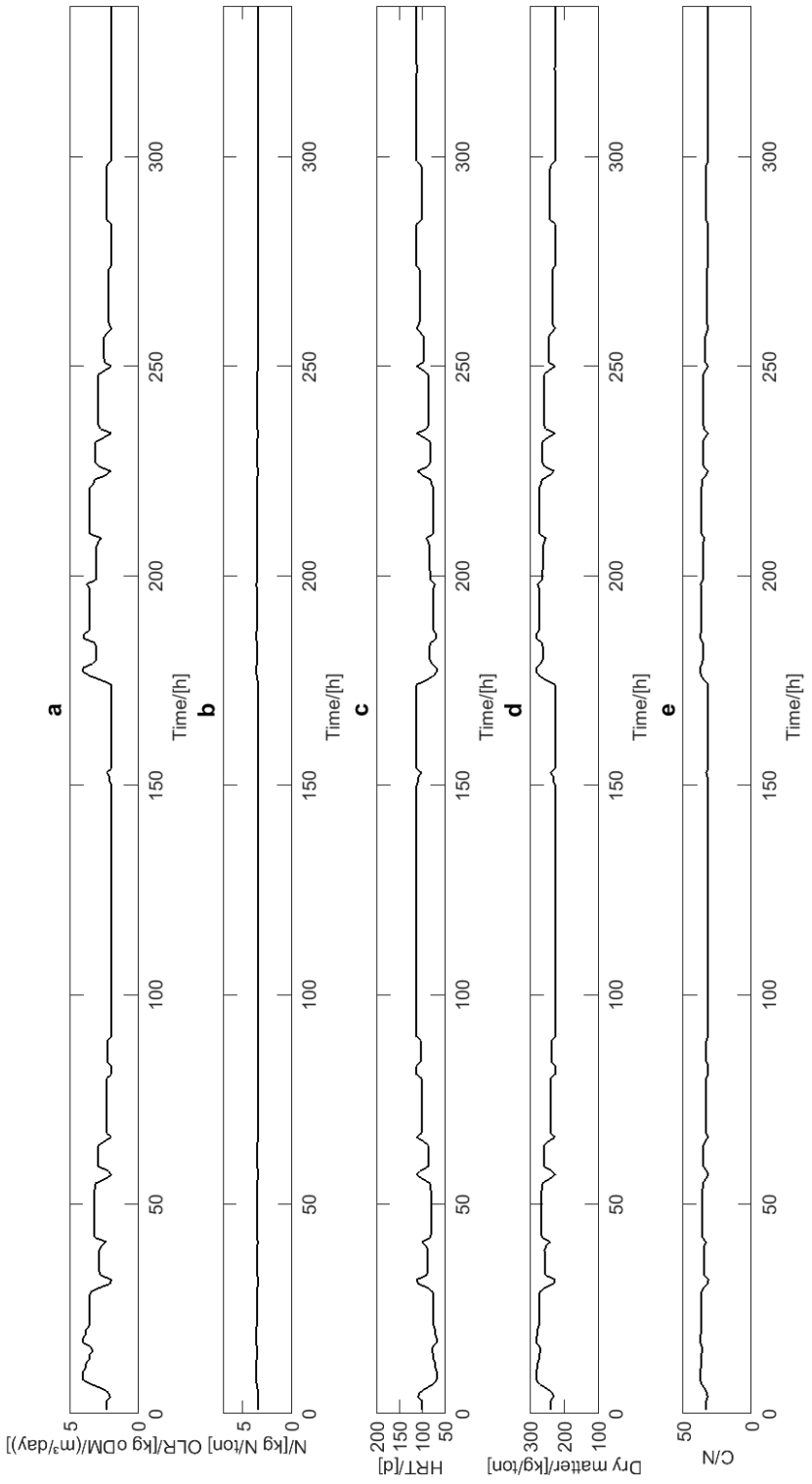


Figure 4.22.: Process parameters feeding on demand a) organic loading rate; b) Nitrogen content; c) Hydraulic residence time; d) Dry matter e) C/N

5. Discussion

5.1. Step response determination with lab reactor

In order to determine whether the step response of maize silage can be determined by a single feeding, a series of measurements in two lab reactors were made. Gas production measurements and methane concentrations for single feedings are presented in Fig. 4.1 and Fig. 4.2. A similar setup was repeated in lab reactor 2 (see Fig. 4.5).

The following observations can be made:

- Biogas production peak occurs immediately after feeding. This behavior has been reported in [161, 175] and observed in full scale biogas plants. This similarity in behavior with a full-scale reactor was one of the criteria to determine the step response (see sec. 3.2.1) and makes the biogas yield curves obtained in the lab reactor a better option to estimate the system step response than the Activity Test (AT, see Fig. 3.2) at which gas production peak occurs 30 hours after feeding.
- Gas production presents a higher second production peak compared with AT test, see Fig. 3.2. A possible explanation is the longer starving period that the lab reactor faced before the feeding, together with the required particle size reduction to avoid pump blockages, see sec. 3.2.1.
- Gas production second peak height and time of occurrence depends on the OLR. After applying the same OLR to both reactors it was found that lab reactor 2 reacts quicker even though both were using inoculum from the same biogas plant. Similar results were found in [76], where two parallel operated lab reactors performed differently and had differences in the microbial structure. Differences were attributed to inoculum heterogeneity and random factors in the setup.
- After the feeding event there is a rapid increase of CO_2 and decrease of CH_4, as previously reported in [75, 161]. This change in biogas composition is explained by the immediate onset of hydrolysis producing organic acids and CO_2 followed by the decomposition of the organic acids into CH_4 thus increasing its concentration. An increase of the VFA could not be determined.
- Accumulated biogas production after 48 hours is similar at the different OLR conditions in lab reactor 1 and reaches about 50% of the theoretical biogas

potential. After this period there is a constant and slow reduction of biogas production. Different cumulative gas productions were reported between lab and full-scale reactor. In general, the reaction in a lab reactor is faster than in full-scale digester [12, 161]. Using maize silage, 50% of its biogas potential was produced at 36h and 51.5h in two full scale digesters [161]. Similar results were obtained in the lab reactor even though a faster reaction was expected due to the required particle size reduction to avoid pump blockages that increases contact area to the microorganism. The reason behind these differences in the reaction time are not clear but attributed to the differences in operating conditions to generate a step response.

- Accumulated biogas production after 48 hours is different at the different OLR conditions in lab reactor 2. This could be explained by an inhibition generated in the reactor when exposed to a relatively high organic shock. There is an increase of the VFA/TIC after the feeding, which returns to the initial level 2 days later.

The resultant biogas production at the same OLR in both reactors is different, even though they have similar starving time. Inoculum and feeding substrates were taken from the same plant but not at the same time. In order to determine whether the source of these variations are the different inoculum, parallel lab reactors must be operated at different conditions to compare the step response.

The third feeding schedule corresponds to a continuous feeding at an OLR of 3.6 every 12 hours. Gas production for continuous feed and its concentration is presented in Fig. 4.3. The purpose of the continuous feeding was to determine whether it is possible to reproduce the biogas production measurements of a continuous feeding schedule by adding step responses of single feedings.

The following observations can be made.

- In single feeding, nutrients like carbohydrates, proteins and fats, are only available at the feeding event and their concentration is continuously reduced by action of hydrolytic acidogenic bacteria. In continuously repeated feeding these are available according to the schedule. In a single feeding there is at first strong hydrolysis/acidogenesis followed by a downstream process to methanogenesis. In continuous feeding there is an alternating cycle of anaerobic digestion stages. This behavior can be observed in the variation of the biogas concentration with time. At the feeding there is an increase of CO_2, which corresponds to hydrolysis, where intermediate compounds are generated. CO_2 concentration is then reduced while at the same time the concentration of CH_4 increases showing the action of methanogens.
- The arithmetic addition of biogas curves obtained with single feeding will not represent the gas production obtained by continuous feeding. This is evident in the last feeding of the continuous series done at 72 hours where the second peak found at different OLR was not present, see Fig. 4.1. There was no evidence of process disturbance which would explain the absence of the second

peak. VFA/TIC varied between 0.156 and 0.176 which is characteristic for a stable system A possible explanation is that the operation conditions in which single feeding was undertaken did not have the same nutrient availability as continuous feeding.

- The single feeding digester was exposed to a long starving time before the feeding which in a continuous feed reactor will not be the case, except when the biogas production must be minimized due to the lower electricity price on weekends. Single feeding step response could be used to estimate the response of the system after a long starving time. In the full-scale digester studied these conditions could not be simulated.

The main conclusion here is that the biogas yield curves for the model should be obtained for the same conditions in which the digester is intended to operate (continuous feeding), and, for that reason, the curves obtained by single feeding are not suited as a representation of step response. The step response was therefore determined from the gas production measurements on the continuous feeding lab rector.

The resultant step response obtained with an exponential fit is presented in Fig. 4.4. Methane content was assumed from the batch test which was considered adequate even with changes of gas concentration over time, because of mixing in the gas storage. The obtained fit with equation 3.1 was intended to be validated, but this later proved impossible, see sec. 5.3.2.2.

The step response obtained with the exponential fit partially satisfied the three criteria imposed to determine system step response, defined in sec. 3.2.1. The criteria were that the step response have similar reaction times and be generated in similar conditions to a full-scale digester. Additionally the step response must be updated as changes in microbial population generating by feeding may modify this response (see sec. 3.2.1). Updating step response is not practical in a lab reactor because it must operate in parallel to a full-scale reactor due to the expected continuous feeding changes in a feeding on demand biogas plant. It was concluded in [76] that variations to microbial structure can also be explained by the different conditions generated in a lab reactor compared with a full-scale digester and for that reason, there is a risk of over-interpreting single reactor data for process optimization.

For the above reasons, the step response of the system was proposed to be measured directly in the plant studied for this work, as described in sec. 3.1, after a non-continuous feeding schedule, but this proved to be difficult. The main advantage of this approach is that the step response is taken from the operating conditions in which the digester is intended to operate, and, in the case that this changes with time it can be updated with the new measurements, see Fig. 4.9. Furthermore, the measurement will also include gas storage effects, due to buffering by the membrane, as possible delays [155].

Two main difficulties arise from this solution

- Only part of the reaction between two feedings can be measured meaning that the behavior in the non-measured period requires manual fitting with an exponential decay. It has been observed (similar results by [13]) that after a feeding there is a period with high biogas yield and dynamics. In the first 12 hours depending on the substrates, a large percentage of the potential gas production is generated. After this time the biogas yield decreases constantly justifying the use of an exponential decay in which the area under the curve will be the remaining biogas production and the time can be assumed as 20 days or longer.
- Generated gas yields must be measured at the gas storage system which must be modified in order to improve the measurements. Similar gas yields to the lab have been found in the commercial plant but only at some digester and storage gas volume levels (Fig. 4.9). Quality of measurements depends on the actual gas volume level, and, for that reason, it is also important to implement a gas management to keep the levels within a range in which they are reliable, see sec. 3.5. In [13] gas production was measured by a flow meter connected at the outlet pipe of a digester with a concrete roof without gas storage capacity. This configuration provides accurate gas yield measurement adequate to calibrate the model, but it is not available in most commercial agricultural biogas plants which have an integrated gas storage capacity and double layer membranes.

The estimation of the step response for pig manure in a full-scale reactor is not practical because of the large amount of digestate produced and high disposal cost. Manure effect in the biogas production is minimal due to its lower biogas production of 35 m^3 at 8.9% DM compared with maize silage 180 m^3 at 33.1% DM. In addition, pig manure quantities were fixed to the minimum amount required to obtain the manure bonus (7.5 m^3/day).

Lab results confirm a low degradation rate of pig manure compared with maize silage [95]. Maize silage and pig manure have similar biogas yields ($m^3/kgoDM$), see Tab. A.1. It was observed in Fig. 4.6, that biogas production is slower because within 48 hours of feeding pig manure only 145/548 = 26% of the gas is produced while in maize silage, see Fig. 4.1, 253/563= 45% is produced which indicates that maize silage is better suited to power on demand feeding programs.

Step response for pig manure should have being obtained with a similar procedure as maize silage but due to a failure in the equipment was not realized. Additional feedings are required at a lower OLR in a continuous feeding schedule to determine the step response.

Manure step response was obtained from a single feeding, see Fig. 4.6, which was not considered a major source error due to its low biogas potential and degradation rate.

5.2. Online monitoring

5.2.1. Sampling parameters

Online monitoring for three combinations of sampling parameters, number of samples n, and sub sample volume $V\_subsample$ is presented in Fig. 4.7.

Digester conditions were kept constant and there was no indication of a process disturbance during the measurement period. This situation was represented by the almost constant VFA/TIC value. VFA and TIC on the other hand have large variations which do not correspond either to variations in the digester conditions, or feeding and make both parameters unsuitable for system characterization. The source of these variations is presumed here to be the difficulty of obtaining exactly the same sample volume of $V = 5ml$ in every measurement. A larger sample will have a larger VFA ($> M_{pH=5\,to\,4.4}$) and a larger TIC ($> M_{pH=5}$) which will be misinterpreted as the device is calibrated for a fixed sample volume.

In equation 2.1 and 2.2 in sec. 2.5.1 the direct effect of sample volume variation can be seen. This is minimized when the ratio VFA/TIC is calculated using equation 2.3. In the 600 ml sample the difference between the maximum and minimum acid consumption $M_{pH=5}$ from starting pH to pH 5 is approx 3 ml. Assuming an extreme scenario in which this difference is only generated by the sample volume, maximum variation of VFA/TIC will be $\pm 0,3/(4 \bullet 3) = \pm 0.025$, about 15% of the mean value but not in a range which could prevent identification of a process disturbance. Calculated values have lower variation, see Tab. 4.3.

Another possible source for variation in TIC and VFA is the remaining sampling errors due to incomplete fulfillment of TOS for practical reasons, see section sec. 2.5.2.

As expected, the configuration with the largest subsample volume (600 ml) and maximum number of subsamples (5) has the lowest standard deviation of VFA/TIC value. All configurations are precise and characterized by low Relative Standard deviation (RSD), implying that any of the configurations can be used. Based on the theory of sampling guidelines sec. 2.5.2 the configuration with the largest subsample volume was selected.

Measurements require a repetition to confirm the selected configuration and validate the results, but, due to the operational expenditure to the biogas plant, this was not possible. This was not seen as critical due to the consistency of the mean values and their low RSD, see Table Tab. 4.3.

Whether a sample is representative or not cannot be assessed from the sample itself but requires knowledge of the sampling procedure in which it has been produced[169]. It is expected that a sample generated from the mixture of subsamples taken over a pumped volume of 2.5 m^3 from the digester is more representative than a sample taken from the tank wall, because of heterogeneity of digester contents. But it is also possible that digester heterogeneity requires a larger pumped volume to truly

represent the digester situation. With the imposed restriction of 4 samples per day a larger pumped volume would not be possible because it involves the central pump operating only for sampling purposes which will not be accepted by the plant operator in the long term. Without modifying plant operation a sample representativity improvement can only be achieved by increasing the sample volume with a larger collecting tank.

Sample representativity can also be increased by implementing on the secondary sampling a representative mass reduction. At the current configuration the 5 ml titration volume is obtained from the filtered sample and send it to the titration cell without involving a composite sampling. It is assumed that the filtered sample is homogeneous and for that reason can be directly pumped.

5.2.2. Measurements in the commercial plant

Modifying the feeding schema did not affect the biological process negatively. There were no relevant variation of VFA/TIC ratio even when feeding was concentrated to a few hours a day. Three feeding transitions are presented see Fig. 4.8, Fig. 4.9 and Fig. 4.10.

It is important to keep in mind that the daily quantity was not modified while its distribution in the day was. Feeding schedule changes were not always planned as can be seen in the variation of the maize silage quantities, due to failures in the solid feeder. Once the operator noticed, he tried to "recover" the feeding, making an additional feeding in the day but keeping the daily feeding quantity constant.

Even the transition to and subsequent operation of the biogas plant on a feeding on demand scenario did not generate an imbalance of the biological process.

A situation of imbalance occurred when the plant was running without changes in the feeding program and the reason is still not clear, see Fig. 4.10. Cobalt concentration was at a low level, see Tab. 4.4, its lowest compared with historical data, but still over the minimum reference values (see [34, 33]). Nevertheless, trace element concentration should be periodically monitored and kept at an operational level, especially if feeding on demand schedules are applied on the system with organic load variation [33]. Addition of trace elements did not produce an immediate reaction in the biogas production; for that reason, it is possible that the imbalance was generated by another source or the bacteria simply required a longer time to recover. It is possible that a faster recovery of the system could have been achieved if the feeding had been reduced earlier avoiding the high accumulation of VFA.

VFA/TIC are not directly related with the concentration or function of methanogenic bacteria. This can be seen in Fig. 4.10, in the period between 20 to 25.03.2018 in which a high activity of methanogenic bacteria converted VFA to methane, but VFA/TIC values were high, oscillating around 0.55. For that reason, behavior trends and no single values are to be considered in system monitoring.

5.3. Gas volume measurements

A set of measurements were done to better understand the influence of solar radiation in the gas storage and determine the operating conditions after modification was made to improve volume measurements.

Previous literature on double layer membranes [155, 151] refers to an operation range at which the measurements are more accurate. Both publications suggest the use of water level gauges instead of the installation of a rope system (rope installed across the diameter of the membrane).

The commercial plant in this study sec. 3.1 has two gas storages, the digester and storage tank, each with a rope system connected to a draw wire sensor in a double conical membrane gas storage. As this is the configuration of many plants in Germany and certainly most of the plants installed by BWE, an improved solution for this volume measurement was researched.

5.3.1. Operational range gas storage.

In order to identify the maximum allowed operational range in the gas storages a series of measurements were made at different gas fill levels, see Fig. 4.11.

It was found that depending on the filling level, two operational ranges can be identified:

- Membranes in contact with each other (on the left of Fig. 4.11): Here gas storage is completely full and gas pressure increases to about 2.5 mbar, as there is no more volume available. Gas temperature is affected due to the heat transferred through contact between the membranes (conduction) and by the pumped air between the membranes which is at ambient temperature. This heat transfer generates large variations of gas temperature due to the changing membrane contact area, which will produce rapid increase in the gas pressure. For example, a temperature variation of approx 22°C was measured at 5:40 am on 23.11.11 that generated a pressure increase and an estimated volume increase of about 30 m^3 (this volume increase could not be measured because gas storage was already full). Sudden over-pressure may reach the level at which the pressure relief valve allows biogas to leave the system with consequential environmental and economic losses.
- Membranes separated (on the right of Fig. 4.11): Here gas temperature is directly correlated with ambient temperature, as heat transfer is due to convection by the air pumped between both membranes. The effect of solar radiation was also investigated (see blue trace) and it does not have a direct impact on the gas volume confirming the results of [151].

Based on these results a maximum allowed operating limit of 90 % of total available volume was selected to avoid membrane contact and the consequent temperature variations.

5.3.2. Gas production calculation

Gas production was calculated with equation 3.30 using a simple moving average over the last hour to estimate $G(30s)_i$, see sec. 3.6.1.

CHP gas consumption was measured by a flow meter delivering values normalized to 0°C, 1 bar. Performing a basic calculation of engine electrical efficiency showed that there was an overestimation of the gas consumption, because the calculated electrical efficiency was only 34%. For the model and year of the engine a higher efficiency was expected. Checking the data sheet of the flow meter revealed that it was not installed properly and the pipe diameter for which it was calibrated was smaller than that of the installation. The manufacturer of this equipment expects an inaccuracy up to 20% in the measured values.

As the engine in the commercial plant is running continuously at full capacity the gas consumption is almost constant but is dependent on the gas methane content.

This gas flow error was considered systematic and was corrected in the gas production estimation by normalizing with the average production generated by the gas model. Normalization avoids the offset between gas production calculated with the volume measurements and CHP consumption, and model prediction measurements. There is still an error because engine gas consumption is also dependent on the methane content which was not corrected based on the model prediction because of the assumption that methane content is constant during the biogas production of each substrate.

Work in the lab identified (see Fig. 4.3) that single feedings generate an immediate increase of CO_2 and decrease of CH_4. Based on the gas quality measurements at the CHP unit (see Fig. 4.10) this effect could not be clearly identified due to the buffer generated by the gas storage.

5.3.2.1. Gas production calculation at original configuration

The first feeding transition was performed without any modification of the gas storage.

Fig. 4.8 shows the calculated biogas production based on gas volume variation in digester and storage. Large gas production variations are observed during the constant feeding period (before 15.8.17) that cannot have been generated due to the feeding. For that reason, it was necessary to modify the gas storage system, as the gas volume estimations assume that the membrane shape is spherical cap and this is not correct, see sec. 3.5.1.

5.3.2.2. Gas production calculation Baur calming system

The Baur company sells a "calming system" consisting of elastic straps installed over the gas storage membrane to get an even gas distribution which is closer to the spherical cap assumption. Two elastic straps and the existing rope divide the membrane into 6 sections. Rope displacements are still measured with the existing draw wire sensor. Before the second feeding transition Fig. 4.9, a Baur system was installed in both storages in the plant.

A large improvement in measurement stability was observed, comparing the system before and after this installation. However, it was also observed that the system response to a single feeding varies with digester and storage filling level. The system has a lower or no response when digester gas storage is empty compared when the digester gas storage is at least partially filled.

During the installation of the straps it was clear that folds in the membrane are a permanent source of error that cannot be avoided. The internal membrane area is fixed and has the same conical shape as the external membrane, which introduces an additional error source due to the volume assumptions of a spherical cap. There is no a folding pattern that allows a better estimation of the membrane shape for volume calculation.

5.3.2.3. Operational parameters verification

Based on the above observation it was decided to improve the gas production calculation by implementing a gas management system, keeping both tanks at the same level. A control philosophy (see sec. 3.5.3) was selected to optimize the gas storage use, avoiding as much as possible low operation levels in both membranes, in which measurements are inaccurate, and high levels where heat is transferred due to membrane contact.

This system worked as expected, allowing gas movements between the membranes and keeping them at the same percentage level as is required.

Gas is transferred from a tank to the other by a pressure gradient generated by a reduction speed of the membrane support fan in one tank. It was then necessary to verify if the implementation of gas management guarantees a minimum pressure and volume to keep the system stable at different gas storage levels.

In the two sets of measurements in both digester and storage, Fig. 4.12 and Fig. 4.13, it could be verified that the selected rpm_{D-MIN} and rpm_{S-MIN} for the gas management provide an air volume between the membranes of over $100m^3/h$ except when the gas storage is fully blocking the air inlet. Air volume over $100m^3/h$ is considered enough because gas is sucked from both gas storages and the average consumption of the engine is only about $120m^3/h$ (considering a correction due to the incorrectly calibrated flow meter).

Air inlet blocking can represent a critical state because a sudden increase of the gas consumption (power on demand) may generate a void that cannot be filled because the fan is blocked. New gas membranes are available which have an air channel welded on the membrane to avoid fan blockage however the investment required for this was not available at the time of this research.

Digester and storage gas pressure P_{gD} and P_{gS} values were always over the minimum restriction of 0.5 mbars during the measuring period.

The current configuration requires modification for the implementation of demand-oriented power generation. In the case that an additional 250 kW engine is installed to enable this, the membrane support fan would not be immediately able to fill the void generated by the change of the gas consumption. A channel would also have to be installed in the air inlet to avoid mechanical blockage at maximum filling level.

Temperature and solar radiation effects were measured in the digester and storage, Fig. 4.14 and Fig. 4.15.

Gas temperature can be accurately estimated based on the outside temperature. A linear fit like Fig. 4.11 can be used to estimate the gas temperature in both digester and storage. Ambient temperature prognoses from the Deutscher Wetterdienst, DWD (Climate Data Center) can be used to estimate the energy content in the gas storage without the necessity of an elaborate model. Only at clear sky conditions i.e. 21.04.2018 there are significant differences in behavior between outside and gas temperature.

Solar radiation was found to have no direct effect on gas temperature, but outside temperature did. These measurements are not in agreement with [155], where a direct relation was measured; the physical construction of the experimental plant in [155] is not known to understand the differences.

Maximum gas fill levels were generated while using the gas management system, but the gas temperature always followed outside temperature, contrary to the observations made in the same plant before the Baur “calming system” was installed, see Fig. 4.11. A possible explanation is that the membrane contact area is reduced due to the elastic straps in the “Baur” installation.

Pumped air has a cooling effect on the external membrane which is warmed by solar radiation. Heat losses can be calculated from the air flow and temperature differences between inlet (outside temperature) and air temperature at the pressure regulating valve. Air flow through the roof space causes temperatures to lag from radiation (see Fig. 4.15).

Air pumped by the supporting fan warms, reducing its density and pressure, and thus pumped volume. For example, in Fig. 4.15 on the 21.04.2018 pumped air at the supporting fan had a temperature increase from 11°C at 6:30 am to 45°C at 5:00 pm. The fan should be sized at the higher temperature to be able to generate higher flows so that the volume of warm air is enough to keep the system stable.

It was also observed that gas temperature in the digester is higher than in the storage. This can be explained by the constant temperature kept in the digester while this and the substrate level are variable in the storage.

5.3.2.4. Gas production calculation with Baur calming system and gas management

Gas management allows more stable measurements, compared with the results obtained without the system. Comparison of gas production between stable gas levels in both tanks controlled by the management system, and that obtained at variable gas volume levels is presented in Fig. 4.16. Gas management system was not active between 16.04.2018 at 10:00 am until 20.04.2018 at 2:00 pm.

During the gas measurements feeding was kept constant to avoid large variations in the gas production calculation. It was found that level variations affect gas production calculations, however this behavior should only correspond to variations in feeding. Gas volume delays are reported at lower gas levels, see [176]. But it can be observed that at different membrane levels such delays are also present. Folding of membranes and flow between them present a complex pneumatic problem, which makes volume determination inaccurate. Response delays are interpreted as a decrease of gas production and fast response as an increase of production.

5.3.2.5. Gas production calculation to estimate maize silage step response

With modified gas storages and the gas management system in place it was intended to measure the step response to maize silage under a feeding schedule to calibrate the system (feeding every 12 hours). Pig manure was fed at 8 am and maize silage daily quantity was divided in two feedings at 9 am and 9 pm. A step response was expected at 9 pm which was less influenced by pig manure. see Fig. 4.17.

The second peak corresponding to the 9 pm feeding could not be identified, and there was no evidence from online monitoring of a process imbalance which would suppress this peak. However, this peak was observed in the lab reactor and generated in the measurements of the second feeding transition when both digester and storage are not empty, see Fig. 4.9. It is possible that the peak was generated, but the buffering effect of gas transfer and subsequent level measured errors caused by folding were enough to obscure the effect of the peak. This implies that membranes only react to larger changes in biogas yields and as the produced gas is divided between both membranes the effect is reduced.

The feeding program was then modified on 11.05.2018 to one feeding per day, generating a good match between measurement and prediction. This confirms that only large gas yields can be properly measured on the gas membranes with the elastic

straps and gas management and this is a limitation for a feeding on demand implementation, because production of small quantities of gas predicted by the model cannot be measured.

As the engine in the test plant operates at constant power, a match between gas production and consumption was not achieved. For that reason gas storage capacity went to high levels (over 90%) where the measuring system is less sensitive to changes, and delays are presented as an increase of gas production.

5.4. Model validation

It was planned to measure step response to maize silage directly in the biogas plant and then validate the model. However it was not possible to measure this directly in biogas production, even after modifications to the gas storage, see sec. 5.3.2.5.

Gas production was calculated with the step response obtained for maize silage and pig manure, see sec. 5.1. Fig. 4.17 on page 105 compares the model prediction (red line) and the biogas production calculated at the biogas plant (green line). Gas production based on the model followed the gas production calculated, but not all the peaks were found, and based on the online monitoring, there was no evidence of a process disturbance that would suppress them. Based on the lab results Fig. 4.3 and the results of [161] an immediate increase of the gas production was expected after feeding. The differences between model prediction and calculated gas production were anticipated in the height and widths of the gas production peaks because it was obtained at different operating conditions.

Comparing Fig. 4.9 with Baur system installed and Fig. 4.17 with Baur and gas management installed, it can be observed that gas production calculation with both systems installed is less sensitive to variations than without them, but the Baur system alone provides less accurate measurements because it depends on filling levels. Model validation was not possible because the gas storage system did not show linear behavior regarding gas volume which makes the calculation of gas production insufficiently accurate for model validation. Model validation could be made with a fixed storage volume and a calibrated flow meter as in [13]. Unfortunately, this configuration is not available in most biogas plants in Germany.

Fig. 4.18 presents the process parameters calculated in the same time period as Fig. 4.17. The first two weeks correspond to constant feeding until 23 04.2018, when the feeding was modified. Although it was agreed with the plant owner that the feeding program would be kept constant in this period, due to malfunction of the solid feeder some feeding was interrupted and later the rate of feeding was increased to keep the daily quantity of maize silage constant. This disturbance later generated variations around design parameters, but such defects are a normal occurrence in biogas plant operation and did not negatively affect the biological process.

In the next four weeks feeding was modified to twice a day. In the middle of this period, for four days, one feeding per day took place and this imposed the highest load $OLR = 5kg\,oDM/(m^3 \cdot day)$ on the system; after that feeding was returned to twice per day. VFA/TIC values remained stable which indicates that the biological process was not affected.

5.5. Feeding program calculation

Even though the model could not be validated in the biogas plant it was used to calculate the feeding program to follow a required load to optimize revenues

In Fig. 4.20 as a result of the implementation of feeding on demand, the use of gas storage was reduced, and a larger range of initial gas storage conditions made it possible to deliver the requested load.

The resultant feeding schedule (see Fig. 4.21) is characterized by two feedings per day concentrating the biogas production in the hours when a maximum power generation is required. A similar schedule was used to measure the step response of the system

The resultant feeding schedule was not implemented in the commercial plant, as the calculation is based on a variable gas consumption which cannot be realized on site, and the high feeding rate required would overfill the gas storage as happened in the model validation, see Fig. 4.17 on page 105 (11.05.2018 - 13.05.2018). In this situation the plant owner would have to take control and reduce feeding to avoid flaring.

In normal operation the biogas plant has been exposed to high OLR for short periods without process imbalance, see Fig. 4.18. In the optimization algorithm a lower OLR was used so a process imbalance was not expected. But, as was observed (see Fig. 4.10), a disturbance can be generated for many reasons and therefore process monitoring is required to be able to react on time.

As presented in Tab. A.1 on page 138 substrate characteristics show a large variation even within the same week. The outcome of this feeding model is totally dependent on substrate characteristics, so that for a practical application it would be necessary to implement a dry matter online measurement.

6. Summary and outlook

Most plant operators of agricultural biogas plants are used to expending only a few hours per day to operate the plant. Greater time expenditures together with additional investment costs and uncertain market conditions are the main restrictions preventing biogas plants from providing flexible power

A large part of the required investment would go to increasing the electrical power generating capacity of the plant. Support from the German government through a flexible power premium is a well-accepted incentive which in most cases covers the cost of purchasing a 2nd engine and allows the plant owners to extend the life span of their existing generator. Often a new engine has a higher electrical efficiency than the older engine, even when operating at half its rated capacity.

The new engines size will depend on the expected flexible operation and the capacity of the plant to provide the engine with the required amount of gas. The traditional alternative to improve this capacity is to increase the existing gas storage and keep a continuous feeding program. As was shown in Fig. 4.20 a larger gas storage does not guarantee that a biogas plant can deliver a requested load, because it will depend on the level of the gas storage at the time the load is requested. Feeding on demand is an alternative to improve potential flexibility, as it increases the range of gas storage levels that can deliver the required load.

This work is focused on technical aspects to overcome problems in maximizing the flexible biogas power potential of existing plants using feeding on demand. The thesis is divided into three areas that are mutually dependent for the successful application of feeding on demand schemes.

- Online monitoring to determine the state of the digester
- Improvement of the gas storage measurement system to guarantee the full utilization of the gas storage, determine gas production feeding schedule and determine step response for model calibration and updates
- Feeding prediction based on a heuristic model

Online monitoring

Currently the number of measurements in most plants is limited to one per day, enough to characterize a continuous digester feed, but insufficient for a biogas plant providing flexible power with feeding on demand. This kind of feeding requires

online supervision of the biological process due to continuous changes of feedstock quality and quantity.

Characterization of intermediate metabolites in the anaerobic digestion process is the standard practice for the determination of the biological process stability [123, 37]. The most commonly used parameters to determine this stability are: total Volatile Fatty Acids (VFA), concentration of each specific acid, in particular acetic and propionic, alkalinity and hydrogen concentration in the liquid phase. Other parameters like pH are less sensitive to VFA concentration changes in a well buffered anaerobic digester [125]. Titrimetric determination of VFA/TIC ratio is the most widely used monitoring method in commercial power plants because of its simplicity, low costs and robustness. The main problem of this method is that the results depend on the sampling method and sample preparation. Samples should be filtered or centrifuged before analysis because titrant consumption increases with the solid contents which would generate an overestimation of the VFA [142]. In most commercial plants samples are simply filtered without defining a minimum particle size. This, and differences in sampling practice, results in samples with a high heterogeneity making the results unreproducible.

Representative sampling plays a major role in the quality of measurements because of the constitutional heterogeneity of digestates. This is characterized by a mixture of different feedstocks such as energy crops, manure or organic wastes at different stages of fermentation. There is also a degree of spatial segregation inside the digester; this is manifested in higher concentrations of acetic acid near the substrate feeding point decreasing with distance [177] and a non-uniform distribution of particle size [178]. Samples taken from the digester wall are not representative of the system [127], and sampling at the wall is the normal practice. A digester has a typical volume of $10^3 m^3$ and the sample required for the analytical measurement has a volume of $10^{-6} m^3$. Therefore, it is important that every mass reduction procedure follows the theory of sampling [179, 143, 144] to be representative.

Now, there is no commercial unit for online measurement of an anaerobic digestion that has a properly representative sampling procedure.

For the implementation of feeding on demand a new online monitoring system was developed and implemented in an agricultural plant to be able to monitor process changes. The device automatically collects a representative digester sample following the guidelines of sampling theory. Samples are filtered to a particle size <0,1 mm and transferred to a customized cell, where they are mixed with distilled water. An automatic titration unit is also controlled by the PLC (Programmable Logic Controller). Titration results are sent automatically to a data base. When the analysis is finished the system cleans itself automatically and keeps the electrode submerged in a KCL-solution (3mol/l) to preserve it for the next titration.

This device was tested to determine the sampling parameters with the lowest standard deviation. It was found that the configuration with the largest subsample volume and maximum number of increments has the lowest standard deviation. Other

configurations are also accurate, which makes them also suitable, but to agree with the sampling theory the larger sample volume was selected.

VFA/TIC values were stable at constant operating condition while, on the other hand, VFA and TIC have large variations which do not correspond either to variations in the digester conditions, or feeding, and make both parameters unsuitable for system characterization. The source of these variations is presumed here to be the difficulty of obtaining the same sample volume of $V = 5ml$ in every measurement. With a view to commercial application, the main lessons learned from this project are the need to improve pump accuracy and implement a continuous volume measurement to reduce error generated by differences in titration volume and to also allow comparison of VFA and TIC.

Monitoring was implemented with an automatic titration unit, but other parameters like redox potential or dissolved hydrogen in the liquid phase can also be measured. A comparison of these will allow determination of the fastest, most precise and most valid parameter.

Increasing the organic loading rate to explore the potential of feeding on demand was not possible in the commercial plant for economic reasons. A further study would be of benefit, where the organic loading rate could be increased to identify up to which rate the system is still stable, and when the online monitoring is able to detect the process disturbance.

Gas storage

Gas holders are only intended to buffer biogas production and store gas during maintenance; in consequence accurate measurement of store gas volumes does not play a major role in commercial plants [16]. For flexible biogas generation more precise information on the filling level of the gas storage is necessary, to determine the capacity of the biogas plant to deliver the required load. Biogas model validation is also required to determine the gas production after a substrate feeding. Work in this study is focused on an air supported double layer storage because it is the most widely used system and was found to be the best suited for flexible power generation [148]. A significant improvement in the gas volume measurements has been achieved with the installation of elastic strips over the gas membrane to ensure an even distribution of gas in its containment [150]. A gas management system was also found to be important to maximize the use of existing gas volume and to improve quality of gas volume measurements. It enables the different gas storages to be kept at the same level by modifying the pressure at the air supporting fan. The procedure of transferring gas between units in a gas storage system was patented in 2009 [153], as was a pressure cascade, recommend in [148], as an alternative, to maximize the use of available gas storage volume. Furthermore, the implementation of active gas management for flexible power production was reported in [154] by the

research project MANBIO, in which minimum and maximum storage volumes were also determined.

In the first set of measurements without any modification of the gas storage it was found that ambient temperature is linearly correlated with gas temperature and not with solar radiation, but this is not valid when the gas membrane is full and touching the outer membrane. At this fill level, narrow temperature peaks of more than 20°C were observed due to a change of heat transfer mechanism from convection to a mixture of conduction and convection. These temperature variations modify the gas volume and can be wrongly interpreted as an increase in biogas production. Gas losses by over-pressure and instability due to fast gas expansions are also possible. To avoid this, the upper operation range of the system was limited to 90%.

In order to determine the gas production of a specific feeding program it is necessary to have accurate measurements of gas volume levels in the plant. After the implementation of the elastic straps an improvement in measurement stability was noticed, but it was also observed that system response varies with digester and storage filing level. The system has a lower or no response when the digester gas storage is empty compared to the filled digester gas storage.

Based on the above observations a gas management system was implemented to modify gas storages volumes. Gas is transferred from one tank to the other by a pressure gradient generated by the reduction of the supporting fan *rpm* in the downstream tank. The aim of the gas management control philosophy was to keep the volume in all gas storages approximately at the same level and to avoid operating ranges where the measurements are not reliable. The operating range of each gas storage was initially fixed between a minimum of 20% and a maximum of 90%. At lower volume levels, the membrane is crumpled, and measurements are inaccurate. At higher volume levels changes in heat exchange processes make measurements unreliable.

Another set of measurements were undertaken with the following objectives.

1. Verify the effect of solar radiation on the gas temperature. This is necessary to determine the volume at standard conditions for further model implementation.
2. Check if the existing equipment is suitable for a power on demand operation.
3. Determine gas management functionality and verify system stability due to the reduction of the fan *rpm*. Fan *rpm* reduction will reduce the gas pressure and air flow between membranes and is necessary to verify, if the proposed reduction satisfy minimum operating values.

The main findings relevant to the proposed objectives were.

Solar radiation: It was verified that there is no direct effect on the gas temperature. Gas temperature can be accurately estimated with the ambient temperature and a linear equation with an offset that must be measured for each storage size and depending whether it is digester or digestates storage (digestate storage temperatures

are lower because they have no heating system). Ambient temperature prognoses from the DWD (Climate Data Center) can be used to estimate the energy content in the gas storage without the necessity of an elaborated model. Only at clear sky conditions there are significant differences in behavior between the outside temperature and gas temperature, see Fig. 4.15 on the 21.04.2018.

Maximum gas filling levels were generated with the gas management system, but the gas temperature always followed outside temperature, contrary to the observations made in the same plant before the elastic straps were installed, see Fig. 4.11. A possible explanation is that the contact area is reduced due to the elastic straps in the "Baur" installation, and the fan cannot generate the pressure when gas is about to be vented because of overfilling.

Existing equipment: The current configuration should be modified for the implementation of demand-oriented power generation. In the case that an additional $250kW$ engine is installed the supporting fan cannot fill the void immediately generated by the change in gas consumption. In this case the external membrane will modify its shape and, depending on the weather, can become unstable. Fan support specification should be modified to increase its flow according to the gas consumption of the engines at maximum capacity. A channel must also be installed in the air inlet to avoid mechanical blockage at maximum filling level.

Even though measurement quality was improved, there was no information on membrane position between the 6 segments generated by the straps and rope, see Fig. 3.13. The inner membrane could move up and down in this area and the rope remained in the same position. It is required to install an additional level measurement in this area, probably a water gauge to minimize this error.

A substantial improvement of the gas volume calculation would be achieved if the internal membrane were elastic and its shape depended on the stored gas pressure. In this way membrane shape would be a spherical cap and its volume could be easily determined. This membrane should be protected with an external membrane which is not supported on air. Air circulation between both membranes has been shown to be a good insulation and should be included in the design.

Another alternative using the existing air supported double layer storage is based on the volume of the external membrane as constant and equal to the volume between the two membranes plus stored gas volume. It consists of the installation of flow meters and thermometers on the external membrane at the inlet and outlet of the air supporting fan. Based on these two flows corrected for air temperature, the volume between both membranes can be calculated and therefore the gas volume. The advantage is that the shape and folding patterns of the internal membrane do not have any impact on the measurements.

Gas management functionality and verification of system stability: The gas management system worked as expected allowing gas movements between the membranes and keeping them at the same level when required. It was verified that the stability of the system is not affected by the reduction of the *rpm* in the digester and storage

membrane support fans to the selected rpm_{D-MIN} and rpm_{S-MIN}. Support fans provide an air volume in each storage of over $100m^3/h$ which is considered sufficient based on the engine consumption which is about $120m^3/h$. Air volume is reduced only when the gas membrane is full and touching the outer membrane blocking the air inlet. Operating pressures were over the minimum restriction of $0.5mbars$.

The gas management system improved measurement accuracy but as the gas is divided between both membranes it was noticed that the rope measurement system only reacted to large variations. On the other hand, the volume variations without gas management depend on the filling level, which is also not acceptable.

As an alternative to improve the measurements an attempt was made to keep gas storage in the storage tank at a constant level, leaving the variations in the gas storage in the digester. However, the reduction of the rpm that reduced the pressure in the storage was not enough to counter the effect of gas production and the level of storage could not be kept constant. A larger pressure gradient would be required, which could be achieved by installing a supporting fan with a higher capacity or further reduction of the rpm of the existing ones. This probably could affect the structural stability of the system for instance under snow load, which should be analyzed in the future.

During the installation of the straps it was clear that folds in the membrane will always be an unavoidable source of error. The internal membrane area is fixed and has the same conical shape as the external membrane, which introduces an additional error source due to the volume assumptions of a spherical cap. There is no folding pattern that allows a better estimation of the membrane shape for volume calculation.

A considerable improvement of the gas volume measurements was achieved in the plant, but the modifications were not enough to determine the gas production of a specific feeding program and validate the developed feeding model.

Feeding model

Current biogas feeding programs are characterized by constant feed rates. As a result, the biogas production is almost constant and can provide base-load generation. It has been shown by [11, 12, 13, 14, 15] that flexible biogas production can be generated by modifying the feeding program of the plant, but intermittent feeding programs are based on model predictions, which require an extensive calibration, which is not always available.

In this work a heuristic biogas model was developed and implemented in an agricultural biogas plant. Biogas production is calculated as the arithmetic addition of the step responses from single feedings and those step responses can be measured in a lab test or directly in the biogas plant after a calibration. The feeding program is the result of the minimum square optimization between the requested load and

power in equivalent gas production. Optimization problem restrictions are; organic loading rate, hydraulic residence time, nitrogen content, maximum dry matter, carbon to nitrogen ratio, gas storage operating range and cost. The model makes a prediction of the gas storage level to keep the system operating at the desired level. As the initial gas storage level is one of the input parameters, the feeding program must be continuously updated, if it differs from a prediction after a specific period.

The implicit assumption here is that a system operating in a certain range of process parameters will be stable and under these conditions the response of the system to feeding events will be similar.

Apart from the mathematical description the major challenge was to determine the step response. Three criteria were imposed to determine the step response of the system

- Similar reaction times as found in the full scale digester.
- Generation of the step response in conditions like the digester
- The microbial population changes with the feeding program, this may change the step response of the system. The method should include the possibility to update the step response over time.

In [14] batch tests were used to determine step response and [120] used the ORGA test to parameterize biogas yield curves. Both tests were not used here, because batch digesters present different conditions to those used in continuous feeding. Intermediate metabolites are accumulated in the batch system while continuous feeding reactors are characterized by dynamic changes due to periodic substrate feeding and product removal

The next alternative to get closer to full scale reactor conditions was a continuous lab reactor. Digestates were taken from the biogas plant used as a test in this work, bleeding this from the pumping system while digestates were pumped between the tanks in order to get a sample as representative as possible. In the configuration used digestates and substrates required a particle reduction to 2 mm to avoid blockage in the pumping system. This lab reactor was used to measure the step response of the substrates although particle reduction increases contact area to the microorganism and can modify its biogas yield.

In order to decrease the effects of previous feeding in the step response the lab digester was not fed for at least 2 days until biogas production was constant at minimum level. The gas production from single maize silage feedings were measured at different OLR. It was found that the generated production curves react immediately after the feeding but instead of generating one peak, two peaks were measured.

Gas concentration in the first peak was higher in CO_2 while second peak was higher in CH_4. This is suggestive of an inhibition due to shock loading after a long starving time. The step response obtained under these conditions does not represent the conditions in a continuous feeding full-scale reactor. Single feeding step response

could be used to estimate the response of the system after a long starving time; for example, on the weekends when it´s required to decrease the gas production due to the low electricity price. However, in the full-scale digester under investigation starvation could not be done.

Based on these results step response should be generated from a continuous feeding digester. It was observed in [161] that a large percentage of the gas production occurs in the first 12 hours after feeding. An 12 hourly calibrated feeding schedule was designed and the step response obtained through a fit with an exponential decay function in which the area under the curve was the total gas production.

Similarly, the step response could be directly measured in the full-scale digester and in the event of step response changes due to changes in the microbial and archaea population, the system could be updated. Furthermore, the step response measured directly in the digester would have the specific behavior of the gas storage as it is to be expected that the membranes generate modifications (response delays).

The main challenge to implementing this in the full-scale reactor is that biogas production cannot be directly measured with a flow meter as in the lab reactor, but must be calculated based on the level changes in the gas storages and consumption of the CHP unit. There are some plants in Germany where the digester has a concrete cover and a direct measurement with a flow meter would then be possible but most of the biogas plants (test plant included) have an integrated gas storage in the digester. This implies that the gas storage system must be well understood and improved to deliver reliable measurements.

A model validation in the commercial plant was not possible because the gas storage system does not exhibit linear behavior regarding gas volume, which biases gas production calculations. Only large gas yields could be properly measured, which makes comparison with the gas yield predicted by the model unacceptably inaccurate.

Even though the model could not be validated in the biogas plant, it was used to calculate the feeding program to follow a revenue maximizing load scheme. A comparison was done between the plant with a continuous feeding program and the plant fed on demand. It was found that in continuous feeding the plant could not deliver the requested load with the existing gas storage capacity. On the other hand the plant following the predicted feeding schedule reduced the use of gas storage and a larger range of initial gas storage levels made delivery of the requested load possible, with process parameter variations kept in the required range, (see Fig. 4.20).

Further practical aspects were identified during the study, i.e. substrate characteristics variation. Substrate characteristics show a large variation even within the same week, see Tab. A.1. The outcome of any model is only as good as the characterization of the input parameters so this presents a problem.

Substrate characteristics in agricultural biogas plants using energy crops are continuously changing due to various factors not in control of the plant operator. Substrates dry matter changes due to

- Position in the silage plate. Depending of the slope of the drainage system in the silage plate, silage effluents will be concentrated decreasing the DM of the substrates
- Farmers harvest different maize varieties to minimize risk. Many kinds of maize are put together in the same silage plate.
- Solid feeders introduce substrate based on weight. In many plants in Germany this equipment is located outside and in the case of heavy rain, water will be collected in the solid feeder and the system will feed less substrate.
- Liquid substrates such as pig manure also depend on the operating conditions in which they are generated. In the case that the stalls have recently been cleaned, lower dry matter is to be expected

For model implementation it will be necessary to have a continuous characterization of the feed substrates, see [14], where microwaves were used to estimate dry matter of solid substrate in the feeding screws and liquids in the pipes.

Trace element requirements also vary according to the imposed organic load to the system [34, 33]. A process imbalance was monitored in the test plant at a continuous feeding schedule which was probably generated by a low concentration of trace elements. Feeding model predictions concentrate feeding in some few hours a day, which may modify bacteria trace element requirements. It is therefore important to implement a continuous control of trace elements and keep these at a minimum desired level according to the expected variations in the organic load.

Feeding on demand practical implementation

The technical aspects presented in this work have reach different stages of development.

For the successful adoption of feeding on demand plant operators must feel comfortable in changing traditional practices by introducing variable feeding. The online monitoring system developed in this work can help to reduce this uncertainty for operators and, with adequate supervision, explore the potential of feeding on demand by operating at higher organic loads with periodic starving to improve flexibility. Online monitoring is now sufficiently developed to be currently available on the market for commercial application, see Fig. 3.8.

Improvements to gas volume determination were achieved by implementing the Baur "calming" system and the gas management system developed in this work. Gas management also guarantees more complete use of the existing gas storage, so that gas is only flared when all storages have reached their maximum level. This is achieved by equal distribution of the produced gas in the available gas storages. The same equipment can be used to empty a gas storage when maintenance works are required for example to change an agitator. Gas management equipment and associated control philosophy were successfully implemented in a full scale plant.

Distributing the gas between the storages also reduces the level of volume variation in each storage, where gas membranes have a buffer effect due to the different folding patterns. This buffer response together with the lower variations in volume level makes the gas production calculation not sufficiently precise to validate the model.

Feeding schedules previously set when the plant was commissioned are now required to be flexible and determined by models that must not involve an elaborated calibration and be simple enough to use by the plant operators. The model developed in this work includes the capacity to update the system response from the plant itself. Model development includes mathematical description in a matrix formulation for faster calculation. Its application in an operational full-scale biogas plant was however not possible even after the gas volume determination improvements detailed in this work which were not able to provide sufficient accuracy in determining measurements of gas production.

The technical solutions discussed here are associated with an additional investment cost and have different degrees of development. Another study would be of use here to evaluate the degree in which the benefits of a larger flexibility compensates the additional investment. Biogas digesters are a means of delivering network services CO_2 neutral and ensuring environmental improvements, however present market conditions do not provide clear market signs that guarantee recovery on investment.

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A. Appendix

A.1. Substrate characteristics test plant

Table A.1.: Substrate characteristics test plant

#	Date	Substrate	DM %	oDM %	Theoretical biogas potential (Baserga)	$\frac{m^3}{kgoDM}$	CH_4	Observations
1	15.09.2016	Maize silage	35.73	95				Analysis for lab reactor 1
2	07.06.2017	Maize silage	33.1	90.6	180	563	52.2	Middle silage plate. Analysis for lab reactor 2
3	07.06.2017	Pig manure stable 1	8.9	73	35	548	55.6	Analysis for lab reactor 2
4	07.06.2017	Pig manure stable 2	5.9	745	24	553	55.4	
5	24.08.2017	Maize silage	43.91	96.59				Analysis for lab reactor 2 (frozen sample)
6	14.11.2017	Maize silage	39,9					End of silage plate
7	15.11.2017	Maize silage	37,7					End of silage plate
8	16.11.2017	Maize silage	37.8					End of silage plate
9	17.11.2017	Maize silage	34.9					End of silage plate

Table A.1.: Substrate characteristics test plant

#	Date	Substrate	DM %	oDM %	Theoretical biogas potential (Baserga)	$\frac{m^3}{kgoDM}$	CH_4	Observations
10	18.11.2017	Maize silage	35.2					End of silage plate
11	19.11.2017	Maize silage	32.4					End of silage plate
12	20.11.2017	Maize silage	29.9					End of silage plate
13	21.11.2017	Maize silage	32.7					End of silage plate
14	06.03.2018	Maize silage	30	90.3	163	561	52.3	Middle silage plate
15	07.03.2018	Maize silage	27.1					Middle silage plate
16	08.03.2018	Maize silage	29.2					Middle silage plate
17	10.03.2018	Maize silage	29.4					Middle silage plate
18	11.03.2018	Maize silage	30.2					Middle silage plate
19	12.03.2018	Maize silage	30.7					Middle silage plate
20	13.03.2018	Maize silage	30.6					Middle silage plate
21	14.03.2018	Maize silage	28,6					Middle silage plate
22	15.03.2018	Maize silage	28,2					Middle silage plate
23	23.04.2018	Maize silage	36,7					Middle silage plate
24	23.04.2018	Pig manure stable 2	3.3%					Stable Wash

A.2. Mathematical model description

The optimization problem is a least-squares-optimization with constraints described in the following equations, see sec. 3.2.2.

$$min \sum_{t} ||P \cdot x - d|| \; with \left\{ \begin{array}{c} A \cdot x \leq b, \\ Aeq \cdot x = beq \\ lb \leq x \leq ub \end{array} \right\} \tag{A.1}$$

Stability and process parameters considered for the anaerobic digestion process are expressed as constraints in the optimization problem. These constraints are presented in Matrices A and Aeq with the limits b and beq. Matrices and vectors are generated by the vertical concatenation of the matrix´s correspondent to the different constraints.

$$A = \left[\begin{array}{c} AN \\ AHRT \\ ADM \\ AOLR \\ -AOLR \\ ACN \\ Vprice \\ AGS \\ -AGS \end{array} \right] \; b = \left[\begin{array}{c} bN \\ bHRT \\ bDM \\ bMaxOLR \\ -bMinOLR \\ bCN \\ bpriceorg \\ bGSMax \\ -bGSMin \end{array} \right] \tag{A.2}$$

$$Aeq = \left[\begin{array}{c} ATE \\ AMS \end{array} \right] \; beq = \left[\begin{array}{c} bTE \\ bMS \end{array} \right]$$

A graphical explanation of the objective function is presented in Fig. A.1.

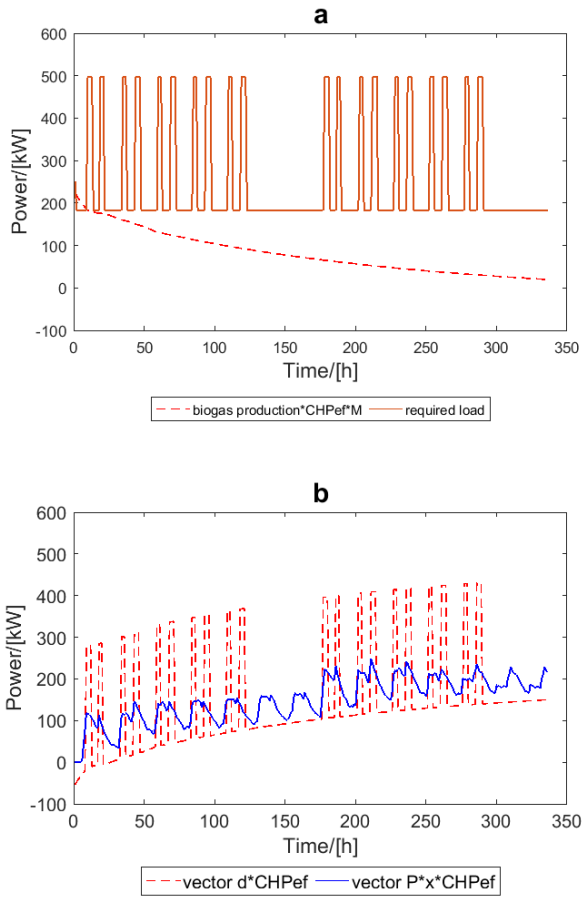

Figure A.1.: Graphical explanation of the objective function a) Represents the conditions before the optimized feeding. Here it is important to note that the biogas production (dotted line) corresponds to feedings made before the optimization interval (biogas production was multiplied by the methane content and engine efficiency to get the same units as the load). Required load is defined by the user according to their specific requirements. b) The difference between the required load and the biogas production is defined by the vector *d*CHPef* (dotted line). The addition of the biogas yield curves, is obtained by the multiplication $P \cdot x$ (d and $P \cdot x$ were both multiplied by the engine efficiency to get the same units as the load). The objective is to minimize the difference between vector d and vector $P \cdot x$, modifying the quantities of the substrates in the vector x, while satisfying the constraints

Description of the Matrices required for the optimization problem.
(All the matrices consider hourly feedings. Based on equations section sec. 3.2.2 and sec. 3.2.3)

Variable	Matrix description
P	$\overbrace{\quad\quad}^{m\cdot t}$ $\overbrace{\quad\quad}^{t}$ $t\left\{\begin{bmatrix} e_{1,1} & & & & \cdot & e_{m,1} & & \\ e_{1,2} & e_{1,1} & & & \cdot & e_{m,2} & e_{m,1} & \\ \cdot & \cdot & e_{1,1} & & \cdot & \cdot & \cdot & \\ e_{1,L_1} & \cdot & \cdot & e_{1,1} & \cdot & \cdot & \cdot & e_{m,1} \\ & e_{1,L_1} & e_{1,L_1-1} & \cdot & e_{1,1} & \cdot & e_{m,t} & e_{m,t-1} & e_{m,2} & e_{m,1} \end{bmatrix}\right.$
Energy matrix: The product of this matrix with the substrate quantities vector x results in the energy equivalent of the gas production (biogas production was multiplied by the methane content). For illustration, the example considers that the energy production time series of substrate 1 has a length that is shorter than the optimization interval $L_1 < t$	
AN	$\overbrace{\quad\quad}^{m\cdot t}$ $\overbrace{\quad\quad}^{t}$ $t\left\{\vphantom{\begin{bmatrix}1\\1\\1\\1\\1\\1\\1\end{bmatrix}}\right.$ $24\left\{\vphantom{\begin{bmatrix}1\\1\\1\\1\end{bmatrix}}\right.$ $\begin{bmatrix} n_1-6 & & & \cdot & & n_m-6 & & \\ n_1-6 & n_1-6 & & \cdot & \cdot & n_m-6 & n_m-6 & \\ \cdot & n_1-6 & & \cdot & \cdot & \cdot & n_m-6 & \\ \cdot & \cdot & n_1-6 & \cdot & \cdot & \cdot & \cdot & n_m-6 \\ n_1-6 & \cdot & n_1-6 & \cdot & \cdot & n_m-6 & \cdot & n_m-6 \\ & n_1-6 & \cdot & \cdot & \cdot & & n_m-6 & \cdot \\ & & \cdot & & \cdot & & & \cdot \\ & & n_1-6 & & \cdot & & & n_m-6 \end{bmatrix}$
Ammonia inhibition matrix: Nitrogen content of each substrate should be given in kg	

Description of the Matrices required for the optimization problem.
(All the matrices consider hourly feedings. Based on equations section sec. 3.2.2 and sec. 3.2.3)

Variable	Matrix description
bN	$t \left\{ \begin{array}{l} 23 \left\{ \begin{array}{l} \left[\begin{array}{c} \sum_{j=1,l=-22}^{m,0} x_{l,j}(6-n_j) \\ \sum_{j=1,l=-21}^{m,0} x_{l,j}(6-n_j) \\ \vdots \\ \sum_{j=1}^{m} x_{0,j}(6-n_j) \end{array} \right. \\ \left. \begin{array}{c} 0 \\ \vdots \\ 0 \end{array} \right] \end{array} \right. \end{array}$

Ammonia inhibition vector: In this vector the total nitrogen added to the digester from the previous feedings is considered. First hour considers nitrogen added from feedings in the last 23 hours. In hour 23 only the feeding previous to the optimization interval is considered. 6 is the maximum nitrogen content in every hour in kg/Mg.

$AHRT$	$\begin{array}{c} \overbrace{}^{m \cdot t} \\ \overbrace{}^{t} \\ t \left\{ \begin{array}{l} 24 \left\{ \begin{array}{l} \left[\begin{array}{cccccccccc} 1 & & & \cdot & & & 1 & & & \\ 1 & 1 & & \cdot & \cdot & & 1 & 1 & & \\ \cdot & 1 & & \cdot & \cdot & & \cdot & 1 & & \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \\ 1 & \cdot & 1 & \cdot & \cdot & \cdot & 1 & \cdot & 1 & \\ & 1 & \cdot & & \cdot & \cdot & & 1 & \cdot & \\ & & \cdot & & & \cdot & & & \cdot & \\ & & 1 & & & \cdot & & & 1 & \end{array} \right. \end{array} \right. \end{array}$

Hydraulic residence time matrix: HRT is defined on a daily basis. The calculation considers substrates fed in a 24 hour period.

Description of the Matrices required for the optimization problem.
(All the matrices consider hourly feedings. Based on equations section sec. 3.2.2 and sec. 3.2.3)

Variable	Matrix description
$bHRT$	$t \left\{ 23 \left\{ \begin{bmatrix} \frac{\text{digestervo1}}{\text{MHRT}} - \sum_{j=1,l=-22}^{m,0} x_{j,l} \\ \frac{\text{digestervo1}}{\text{MHRT}} - \sum_{j=1,l=-21}^{m,0} x_{j,l} \\ \vdots \\ \frac{\text{digestervo1}}{\text{MHRT}} - \sum_{j=1}^{m} x_{j,0} \\ \frac{\text{digestervo1}}{\text{MHRT}} \\ \vdots \\ \frac{\text{digestervo1}}{\text{MHRT}} \end{bmatrix} \right. \right.$
Hydraulic residence time vector: This vector considers the quantity of the previous feedings. $MHRT$ is defined as 60 days.	
$AOLR$	$t \left\{ 24 \left\{ \begin{bmatrix} odm_1 & & & \cdots & & odm_m & & \\ odm_1 & odm_1 & & \cdots & & odm_m & odm_m & \\ \cdot & odm_1 & & \cdots & & \cdot & odm_m & \\ \cdot & \cdot & odm_1 & \cdots & \cdot & \cdot & \cdot & odm_m \\ odm_1 & \cdot & odm_1 & \cdots & \cdot & odm_m & \cdot & odm_m \\ & odm_1 & \cdot & \cdots & \cdot & & odm_m & \cdot \\ & & \cdot & & \cdot & & & \cdot \\ & & odm_1 & & \cdot & & & odm_m \end{bmatrix} \right. \right.$ $\quad m \cdot t$ (over t)
Organic loading rate matrix: Matrix elements are the organic dry matter of each substrate in kg per Mg fresh material.	

Description of the Matrices required for the optimization problem.
(All the matrices consider hourly feedings. Based on equations section sec. 3.2.2 and sec. 3.2.3)

Variable	Matrix description
$bMaxOLR$ $bMinOLR$	$t \left\{ 23 \left\{ \begin{bmatrix} \text{digestervo1} \cdot \text{MaxOLR} - \sum_{j=1,l=-22}^{m,0} x_{j,l} \cdot odm_j \\ \text{digestervo1} \cdot \text{MaxOLR} - \sum_{j=1,l=-21}^{m,0} x_{j,l} \cdot odm_j \\ \vdots \\ \text{digestervo1} \cdot \text{MaxOLR} - \sum_{j=1}^{m} x_{j,0} \cdot odm_j \\ \text{digestervo1} \cdot \text{MaxOLR} \\ \vdots \\ \text{digestervo1} \cdot \text{MaxOLR} \end{bmatrix} \right. \right.$

Organic loading rate vector: In this vector the organic fraction weight of previous feedings is considered. $bMinOLR$ is in the same form but $MaxOLR$ is replaced by $MinOLR$. $MaxOLR$ and $MinOLR$ were set to 4 and $2kg\,oDM/(m^3 \cdot day)$ respectively.

ADM

$$t \left\{ 24 \left\{ \overbrace{\begin{bmatrix} dm_1 - D_{ref} & & & & & & dm_m - D_{ref} & & \\ dm_1 - D_{ref} & dm_1 - D_{ref} & & & & & dm_m - D_{ref} & dm_m - D_{ref} & \\ \vdots & dm_1 - D_{ref} & & \ddots & & & \vdots & dm_m - D_{ref} & \\ \vdots & \vdots & dm_1 - D_{ref} & \cdots & \cdots & & \vdots & \vdots & dm_m - D_{ref} \\ dm_1 - D_{ref} & \vdots & dm_1 - D_{ref} & & \ddots & & dm_m - D_{ref} & \vdots & dm_m - D_{ref} \\ & dm_1 - D_{ref} & \vdots & & & & & dm_m - D_{ref} & \vdots \\ & & \vdots & & & & & & \vdots \\ & & dm_1 - D_{ref} & & & & & & dm_m - D_{ref} \end{bmatrix}}^{t} \right. \right.$$
$$\overbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}^{m \cdot t}$$

Dry matter matrix: Matrix elements are the dry matter of each substrate in kg per Mg fresh material. D_{ref} is defined as $270kg/Mg$

Description of the Matrices required for the optimization problem.
(All the matrices consider hourly feedings. Based on equations section sec. 3.2.2 and sec. 3.2.3)

Variable	Matrix description
bDM	$t \left\{ 23 \left\{ \begin{bmatrix} \sum_{l=-22,j=1}^{0,m} x_{l,j}(D_{ref} - dm_j) \\ \sum_{l=-21,j=1}^{0,m} x_{l,j}(D_{ref} - dm_j) \\ \vdots \\ \sum_{j=1}^{m} x_{0,j}(D_{ref} - dm_j) \\ 0 \\ \vdots \\ 0 \end{bmatrix} \right. \right.$

Dry matter vector: In this vector the dry matter weight of previous feedings is considered.

ACN	$t \left\{ 24 \left\{ \begin{bmatrix} c_1 - C/N_{ref} \cdot n_1 & & & & c_m - C/N_{ref} \cdot n_m & & \\ c_1 - C/N_{ref} \cdot n_1 & c_1 - C/N_{ref} \cdot n_1 & & & c_m - C/N_{ref} \cdot n_m & c_m - C/N_{ref} \cdot n_m & \\ \vdots & c_1 - C/N_{ref} \cdot n_1 & \ddots & & \vdots & c_m - C/N_{ref} \cdot n_m & \\ \vdots & \vdots & c_1 - C/N_{ref} \cdot n_1 & \cdots & \vdots & \vdots & c_m - C/N_{ref} \cdot n_m \\ c_1 - C/N_{ref} \cdot n_1 & \vdots & c_1 - C/N_{ref} \cdot n_1 & \ddots & c_m - C/N_{ref} \cdot n_m & \vdots & c_m - C/N_{ref} \cdot n_m \\ & c_1 - C/N_{ref} \cdot n_1 & \vdots & \ddots & & c_m - C/N_{ref} \cdot n_m & \vdots \\ & & \vdots & \ddots & & & \vdots \\ & & c_1 - C/N_{ref} \cdot n_1 & & & & c_m - C/N_{ref} \cdot n_m \end{bmatrix} \right. \right.$ $m \cdot t$ t

C/N Ratio matrix: $C/Nref$ is defined as 25. Matrix elements should be in kg.

bCN	$t \left\{ 23 \left\{ \begin{bmatrix} \sum_{j=1,l=-22}^{m,0} x_{l,j}(c_j - C/N_{ref} \cdot n_j) \\ \sum_{j=1,l=-21}^{m,0} x_{l,j}(c_j - C/N_{ref} \cdot n_j) \\ \vdots \\ \sum_{j=1}^{m} x_{0,j}(c_j - C/N_{ref} \cdot n_j) \\ 0 \\ \vdots \\ 0 \end{bmatrix} \right. \right.$

C/N Ratio vector: $C/Nref$ is defined as 25. Here the carbon and nitrogen content of the feedings before the optimization interval is considered.

Description of the Matrices required for the optimization problem.
(All the matrices consider hourly feedings. Based on equations section sec. 3.2.2 and sec. 3.2.3)

Variable	Matrix description
$Vprice$	$m \cdot t$; t; $[p_1 \quad p_1 \quad \cdot \quad p_1 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad p_m \quad p_m \quad \cdot \quad p_m]$

Price vector: The product from this vector with the substrate quantities vector x results in the substrates price in the feeding interval. For the optimization it is considered that this price must not be higher than the price when the plant was continuously feeding $bpriceorg$. $Vprice \cdot x < bpriceorg$

AMS	$m \cdot t$; t, q substrate; t; 24; $\begin{bmatrix} 0 & & & 1 & & & 0 & & \\ 0 & 0 & & 1 & 1 & & 0 & 0 & \\ \cdot & 0 & & \cdot & 1 & & \cdot & 0 & \\ \cdot & \cdot & 0 & \cdot & \cdot & 1 & \cdot & \cdot & 0 \\ 0 & \cdot & 0 & 1 & \cdot & 1 & 0 & \cdot & 0 \\ & 0 & \cdot & & 1 & \cdot & & 0 & \cdot \\ & & \cdot & & & \cdot & & & \cdot \\ & & 0 & & & 1 & & & 0 \end{bmatrix}$

Minimum substrate quantity matrix: In this case it is considered that substrate q has a minimum restriction. The product from this matrix with the substrate quantities vector x, results in the substrates quantity of substrate q fed in 24 hours in the feeding interval.

Description of the Matrices required for the optimization problem.
(All the matrices consider hourly feedings. Based on equations section sec. 3.2.2 and sec. 3.2.3)

Variable	Matrix description
bMS	$t \left\{ 23 \left\{ \begin{bmatrix} QR_r - \sum_{l=-22}^{0} x_{r,l} \\ QR_r - \sum_{l=-21}^{0} x_{r,l} \\ \cdot \\ \cdot \\ QR_r - x_{r,0} \\ QR_r \\ \cdot \\ QR_r \end{bmatrix} \right. \right.$

Minimum substrate quantity vector: Substrate quantities from the substrate q fed previous to the optimization interval are considered in this vector. Maximum quantity of substrate q is defined by QRr.

AGS

$$t \left\{ \begin{bmatrix} g_{1,1} & & & & \cdot & g_{m,1} & & \\ g_{1,1}+g_{1,2} & g_{1,1} & & & \cdot & g_{m,1}+g_{m,2} & g_{m,1} & \\ \cdot & \cdot & g_{1,1} & & \cdot & \cdot & \cdot & \\ \sum_{l=1}^{L_1} g_{1,l} & \cdot & \cdot & g_{1,1} & \cdot & \cdot & \cdot & g_{m,1} \\ & \sum_{l=1}^{L_1} g_{1,l} & \sum_{l=1}^{L_1-1} g_{1,l} & \cdot \quad g_{1,1} \quad \cdot & & \sum_{l=1}^{t} g_{m,l} & \sum_{l=1}^{t-1} g_{m,l} & g_{m,1} \end{bmatrix} \right.$$

$m \cdot t$ (over columns); t (over columns)

if
$L_1 < t$
$L_m \geq t$

Gas storage range matrix: The product from this matrix with the substrate quantities vector x results in the accumulated gas production from a feeding schedule in the optimization interval. For illustration, the example considers that the gas production time series of substrate 1 (step response) has a length that is shorter than the optimization interval $L_1 < t$.

Description of the Matrices required for the optimization problem.
(All the matrices consider hourly feedings. Based on equations section sec. 3.2.2 and sec. 3.2.3)

Variable	Matrix description
$bGSMax$ $bGSMin$	$t \left\{ \begin{bmatrix} MaxS/_{\mathrm{CF(T,P)_1}} - GS_0 + d_1/M_0 \\ MaxS/_{\mathrm{CF(T,P)_2}} - GS_0 + (d_1+d_2)/M_0 \\ \cdot \\ \cdot \\ MaxS/_{\mathrm{CF(T,P)_i}} - GS_0 + \sum_{l=1}^{i} d_l/M_0 \\ \cdot \\ MaxS/_{\mathrm{CF(T,P)_t}} - GS_0 + \sum_{l=1}^{t} d_l/M_0 \end{bmatrix} \right.$ $if\ MaxS/_{\mathrm{CF(T,P)_i}} - GS_0 + \sum_{l=1}^{i} d_l/M_0 < 0$ $then, MaxS/_{\mathrm{CF(T,P)_i}} - GS_0 + \sum_{l=1}^{i} d_l/M_0 = 0$

Gas storage range vector: This vector considers the gas consumption and gas production from feedings before the optimization interval in the vector d. $MaxS$ is the maximum allowed gas storage, $CF(T,P)_i$ is the volume correction factor, GS_0 and M_0 are the initial gas storage volume and methane content.

ATE

$$\overbrace{\left[\underbrace{\sum_{k=1}^{L_1} e_{l,k} \quad \sum_{k=1}^{L_1} e_{l,k}}_{t} \quad \underbrace{\sum_{k=1}^{L_1-1} e_{l,k} \quad \cdot \quad \sum_{k=1}^{1} e_{l,k}}_{L_1} \quad \cdots \quad \sum_{k=1}^{t} e_{m,k} \quad \sum_{k=1}^{t-1} e_{m,k} \quad \cdot \quad \sum_{k=1}^{1} e_{m,k}\right]}^{m \cdot t}$$

$$if \quad \begin{matrix} L_1 < t \\ L_m \geq t \end{matrix}$$

Total energy vector: The product from this vector with the substrate quantities vector x results in the substrates energy content in the feeding interval. For the optimization, it is considered that this energy must equal the energy required to deliver the requested load in the optimization interval bTE. $ATE \cdot x = bTE$

A.3. Thesis

A.3.1. Motivation and Objectives

The increasing share of alternating renewable energies from wind and solar introduces the necessity of flexible power generation to reduce the gap between production and demand. Flexible power generation can be provided by fossil fuels, but in the long term it should be provided by renewable energies. Biogas plants can provide flexible power generation in a wide range but the existing plants are designed to provide base load only.

Flexible power generation can be improved by increasing gas storage capacity, but the ability to provide a load profile is limited. A further improvement can be achieved by changing the current continuous feeding to feeding on demand where the biogas plant is fed according to load requirements.

Flexible operation is required for the successful implementation of biogas plants in countries where there are no fixed feed-in tariffs support schemes and the plants are forced to produce when the electricity price is high in order to be economically feasible.

In order to improve the capacity of an existing plant to deliver power on demand the following three technical aspects were identified as objectives for this work:

- Develop a heuristic biogas model that enables the generation of feeding programs restricted by commonly used parameters of the biogas industry. Feeding programs should optimize the usage of the existing gas storage allowing the plant to deliver a wider range of loads as well as to provide system services, such as offering control power in balancing markets.
- Develop an online monitoring system that allows the continuous supervision of the biological process. Sampling acquisition should be representative for the digester, automatic, and able to generate high data density. Online measurements should be adequate to characterize the stability of the anaerobic digestion process.
- Improve gas storage volume measurements and define operating ranges where the measurements are accurate and weather effects are minimized.

This required consideration and development of the following main topics:

1. Develop an optimization algorithm with the objective to obtain a feedstock feeding schedule whose biogas production follows a required load. This algorithm minimizes the required gas storage capacity, while keeping operational parameters like organic loading rate, hydraulic residence time, nitrogen content, maximum dry matter, carbon to nitrogen ratio, gas storage operating level and cost within a desired range.

2. Determine the best suited biogas yield curves for the algorithm based on measurements in a laboratory and full scale biogas reactors. Identify the criteria to determine if the obtained biogas yield curves represent the full scale digester conditions.
3. Develop a sampling system that generates representative samples of the digester to improve the accuracy of the online monitoring based on the theory of sampling.
4. Calibrate the online monitoring to increase sampling representativity in a full scale biogas plant.
5. Develop a gas management system and a control philosophy to optimize the use of the existing gas storage and improve volume measurement accuracy.
6. Measure the main factors affecting the air supported double layer gas storage (the most used system in biogas plants in Germany), to improve measurement quality.
7. Determine the degree of suitability of existing gas storage equipment in the test plant for power on demand. Gas is transferred from one storage to the other by a pressure gradient generated by speed reduction of the membrane support fan in one storage. It is then necessary to verify if the implementation of gas management guarantees a minimum pressure and volume to keep the system stable at different gas storage levels.

A.3.2. Main Results

The main results of this thesis are described as follow:

1. It was shown in laboratory reactors that the biogas curves obtained by a single feeding, simulating a batch test, do not represent the behavior of a full scale digester, due to differences in the biogas yield kinetics. The curves obtained in the lab from a continuous feeding schedule were closer to the behavior observed at the full scale reactor used in this work. But, as has been reported, reaction times are different between lab reactor and full scale [12, 161]. Because of this it was concluded that the curves should be obtained directly from the full scale digester. Furthermore, as observed in the lab reactor, biogas production curves vary with operating conditions and it is to be expected that changes generated in the feeding may affect the microbial activity and therefore biogas yield. These changes are not likely to be simulated in the lab reactor
2. Mathematical formulation of the optimization algorithm was achieved and tested in a theoretical scenario, but for its implementation further improvements of gas volume measurement are required to evaluate the gas production. The proposed mathematical model has the property that the step response of the system can be updated based on measurements done in the same plant as yield is expected to change with feeding changes.

3. Online monitoring was successfully implemented in a full scale biogas plant enabling the representative sampling from heterogeneous liquid systems, e.g. biogas slurry, where the sample size is 10^{-9} of the digestate volume. The proof of suitability of the system was given in a 2 years operational phase on an agricultural biogas plant. Process stability, especially when operating the biogas plant by feeding-on-demand, could be frequently and reliably analyzed.
4. Online monitoring device was configured to determine the sampling parameters with the lowest standard deviation. It was found that the configuration with the largest subsample volume and maximum number of increments had the lowest standard deviation. Other configurations are also accurate, which makes them also suitable, but to agree with sampling theory the larger sample volume was selected.
5. Solar radiation was found to have no direct effect on gas temperature, but outside temperature did. These measurements are not in agreement with [155], where a direct relation was measured, however the physical construction of the experimental plant in [155] is not known to understand the differences. Gas temperature can be calculated by a linear relation with the outside temperature without an elaborated model, this depends on the digester size.
6. Gas storage behavior changes with filling levels. At high filling levels when the gas storage and weather protection membranes start to get in contact the gas temperature has high variations due to the heat transfer between the membranes. Based on this finding the maximum allowed gas storage level must be restricted, because temperature variations also create volume variations, generating a possible gas loss. At lower filling levels there is a linear relation between outside and gas temperature. When one of the gas storages approaches am empty condition estimations of gas production are incorrect due to the membrane folding.
7. Based on the above observation a control philosophy was implemented to keep gas storages at the same percentage level. This was successfully implemented in a full scale plant to optimize the gas storage use, avoiding as much as possible low operation levels in the membranes, in which measurements are inaccurate, and high levels where heat is transferred due to membrane contact.
8. The assumption that the internal membrane shape is a spherical cap used to calculate the gas storage volume is not correct. The manufactured shape of the internal membrane is fixed and conical and at lower volume levels is deformed by folding. In addition pressure variations are small. Elastic straps were installed to distribute the gas equally over the digester area but between the straps variations of gas volume generate membrane movements that cannot be detected. Volume measurements always have a response delay and this effect was observed at different filling levels. In that sense the volume measurements are an indication but not accurate enough to determine the gas production of the digester.

9. Only large gas yields can be properly measured with the elastics straps and gas management system, as the gas produced is divided between both gas storages. This is a limitation for a feeding on demand implementation, because production of gas from small feeding quantities, predicted by the model, cannot be measured. A feeding schedule to measure the step response of the digester was applied at both a lab reactor and the full scale reactor. In the lab reactor immediately after the feeding there is a peak in the biogas production, but in the full scale reactor only at certain filling levels. There was no evidence from online monitoring of a process imbalance which would suppress this peak. Feeding schedule was then modified, concentrating the daily feeding quantity in a single feeding, generating a good match between measurement and prediction, confirming that only large gas yield can be measured.
10. Modifying the feeding schema did not affect the biological process negatively. There were no relevant variations of VFA/TIC ratio even when feeding was concentrated to a few hours a day. The feeding daily quantity was not modified while its distribution in the day was, keeping the same OLR.
11. The current gas storage equipment configuration requires modification for the implementation of demand-oriented power generation. In the case that an additional 250 kW engine is installed increasing the gas volume consumption by 130 m^3, the membrane support fan would not be immediately able to fill the void generated by the change of gas consumption. A channel would also have to be installed in the air inlet to avoid mechanical blockage at maximum filling level. Pumped air between membranes gets warm decreasing the fan capacity. Fan should be sized at the higher temperature to be able to generate higher flows so that the volume of warmer air is enough to keep the system stable.
12. Different speed variation in the air supporting fan was required in the digester and storage to move the gas between membranes. The difference was due to the different diameters of the gas membranes. It was verified that the selected fan rpm reduction allowed the system to remain over the minimum pressure and volume criteria.

A.3.3. Scientific evaluation of the results

The main relevance of this work is to provide technical solutions to the implementation of feeding on demand suited and tested in full scale biogas plant.

1. A full automatic online monitoring was successfully implemented in a full scale plant. The system was able to detect process disturbance and monitor the feeding changes. External lab results validated the indication given by online monitoring, which allows a high density of data to check the process evolution. The results are available immediately allowing a faster reaction time without waiting the 2 or 3 days required by the laboratory. Online monitoring allows a

safer operation in a feeding on demand scenario because any major disturbance can be identified and actions can be taken to recover the process decreasing the risk to the plant owner. Online monitoring was patented and developed to the stage of a commercial product.

2. For the successful adoption of feeding on demand plant operators must feel comfortable in changing traditional practices by introducing variable feeding. The online monitoring system developed in this work can help to reduce this uncertainty for operators and, with adequate supervision, explore the potential of feeding on demand by operating at higher organic loads with periodic starving to improve flexibility.
3. Feeding schedules previously set when the plant was commissioned are now required to be flexible and determined by models that must not involve an elaborated calibration and be simple enough for use by the plant operators. The model developed in this work includes the capacity to update the system response from measurements generated in the plant itself. Model development includes mathematical description in a matrix formulation for faster calculation. Its application in an operational full-scale biogas plant was however not possible even after the gas volume determination improvements detailed in this work, as these were not able to provide sufficient accuracy in determining measurements of gas production. Model validation could be made with a fixed storage volume and a calibrated flow meter as in [13]. Unfortunately, this configuration is not available in most biogas plants in Germany. Technical solutions are proposed to improve the gas volume measurements in double layer membranes.
4. Flexible power generation depends on the optimum use of the existing gas volume. The gas management develop here maximizes the gas volume utilization.

A.3.4. General meaning of the results

For the implementation of flexible power generation in biogas plants the following practical aspects can be identified.

1. Substrate characteristics in agricultural biogas plants using energy crops are continuously changing due to various factors not in control of the plant operator. A continuous measurement for the dry matter is recommended to improve model predictions.
2. Trace element requirements also vary according to the imposed organic load to the system [34, 33]. A process imbalance was monitored in the test plant at a continuous feeding schedule, probably generated by a low concentration of trace elements. Feeding model predictions concentrate feeding in some few hours a day, which may modify bacteria trace element requirements. It is therefore important to implement a continuous control of trace elements and

keep these at a minimum desired level according to the expected variations in the organic load.

3. Improvements of gas volume determination were achieved by implementing the Bauer "calming" system (elastic straps), and the gas management system developed in this work. Gas management also guarantees more complete use of the existing gas storage, so that gas is only flared when all storages have reached their maximum level. This is achieved by equal distribution of the produced gas in the available gas storages. The same equipment can be used to empty a gas storage when maintenance works are required, for example to change an agitator.
4. The procedure used to measure the gas storage in this work can be used in other biogas plants to determine if equipment is suitable for a planned degree of flexible generation.

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Selbstständigkeitserklärung

Ich erkläre, dass ich die eingereichte Dissertation selbständig und ohne fremde Hilfe verfasst, andere als die von mir angegebenen Quellen und Hilfsmittel nicht benutzt und die den benutzten Werken wörtlich oder inhaltlich entnommenen Stellen als solche kenntlich gemacht habe. Die vorgelegte Dissertation wurde bisher weder im Ausland noch im Inland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

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